Supporting Information for:

Decomposition of Ruthenium Olefin Metathesis Catalysts

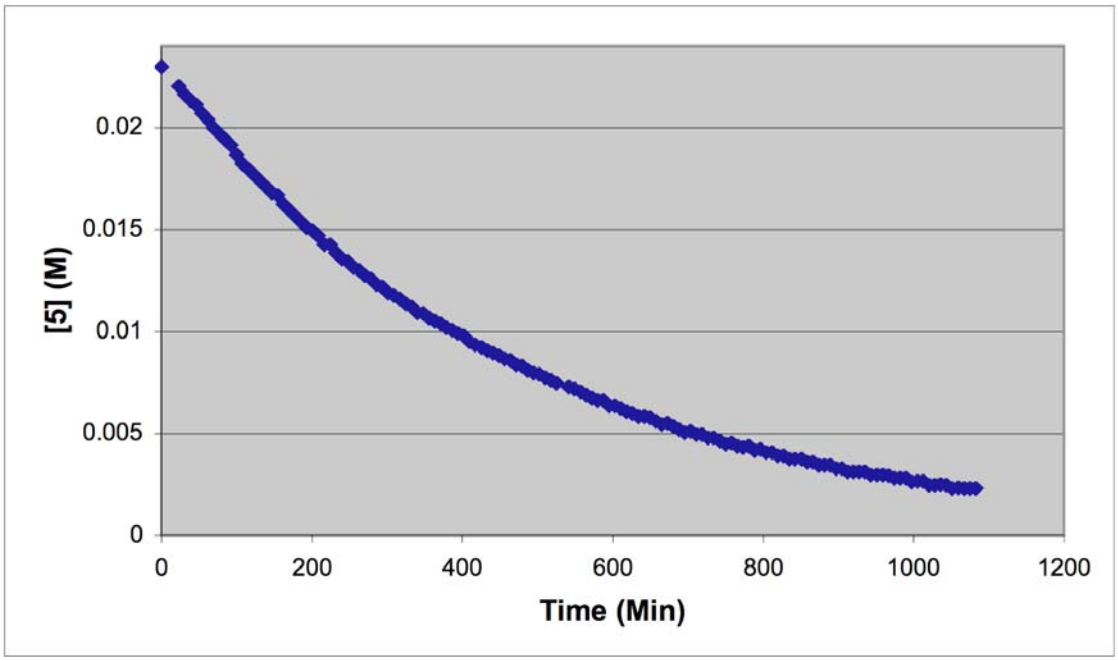
*Soon Hyeok Hong, Anna G. Wenzel,[†] Tina T. Salguero,[‡] Michael W. Day and Robert H. Grubbs**

The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

[†] Current Address: Joint Science Department; Claremont McKenna, Pitzer and Scripps Colleges; Claremont, California 91711.

[‡] Current Address: HRL Laboratories, LLC; Malibu, California 90265-4797.

Chart S.1. Decomposition of **5**.



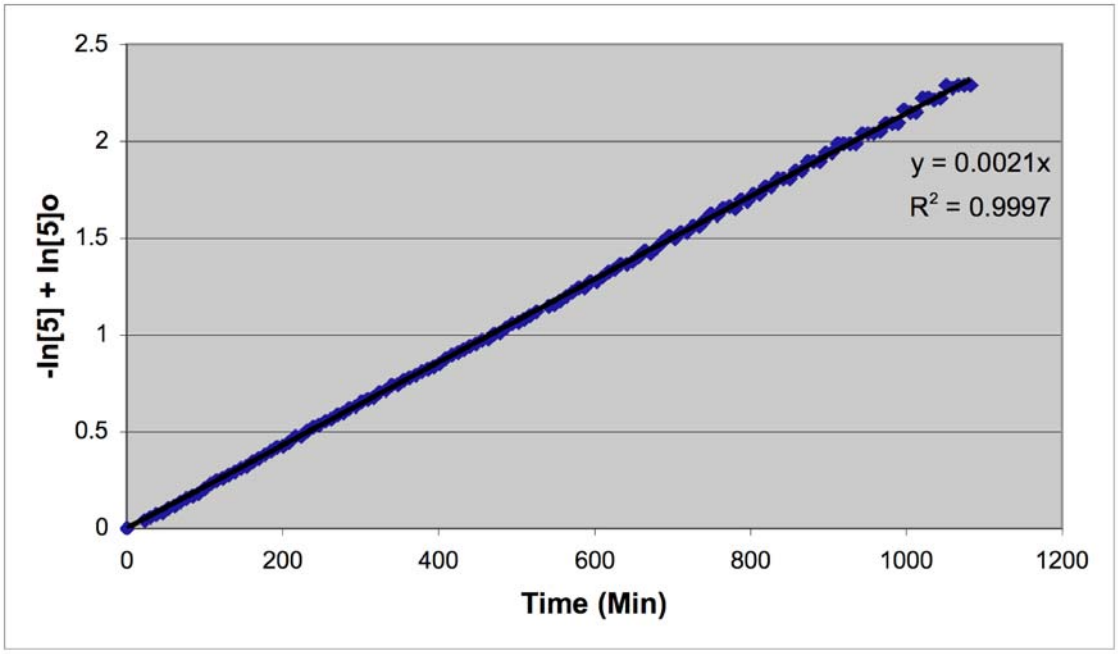
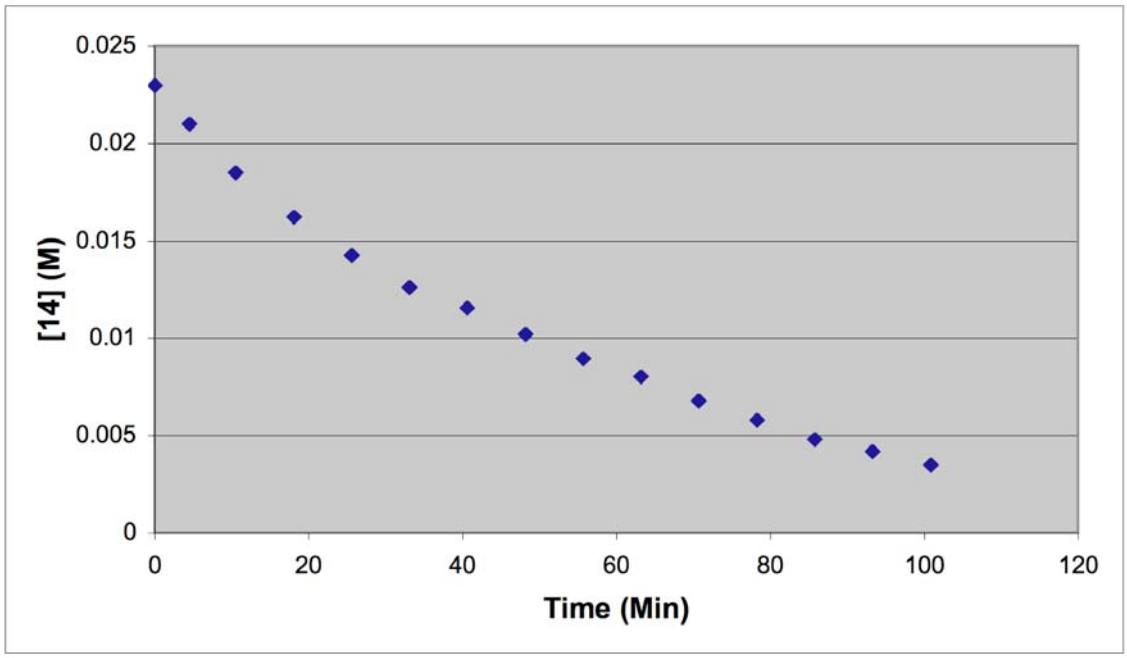


Chart S.2. Decomposition of **14**.



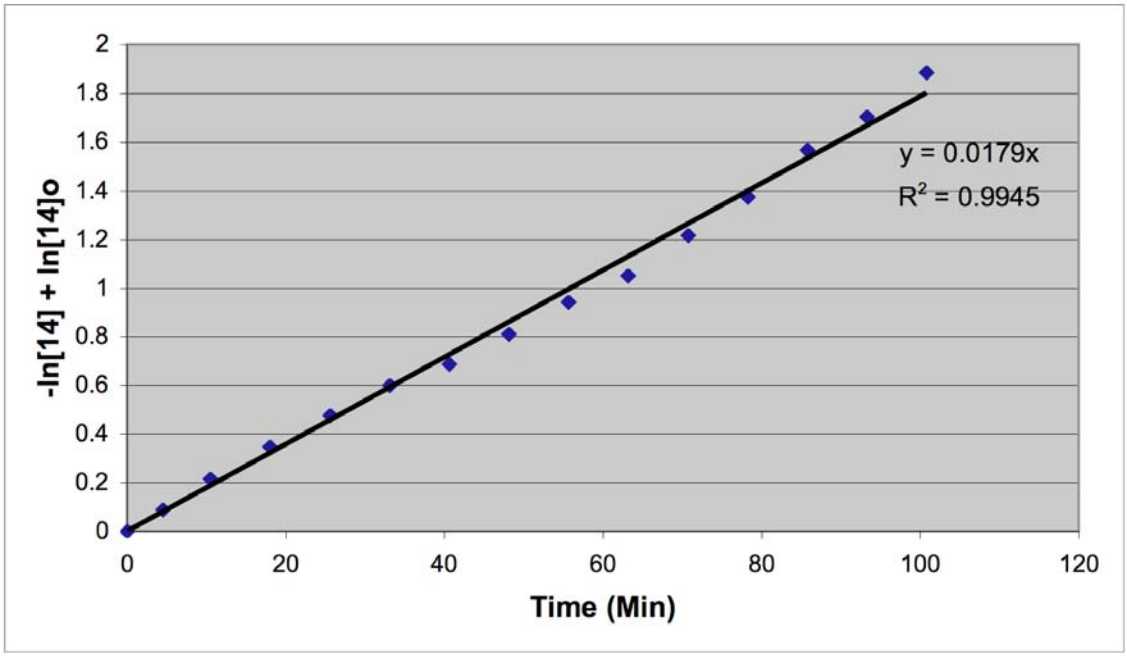
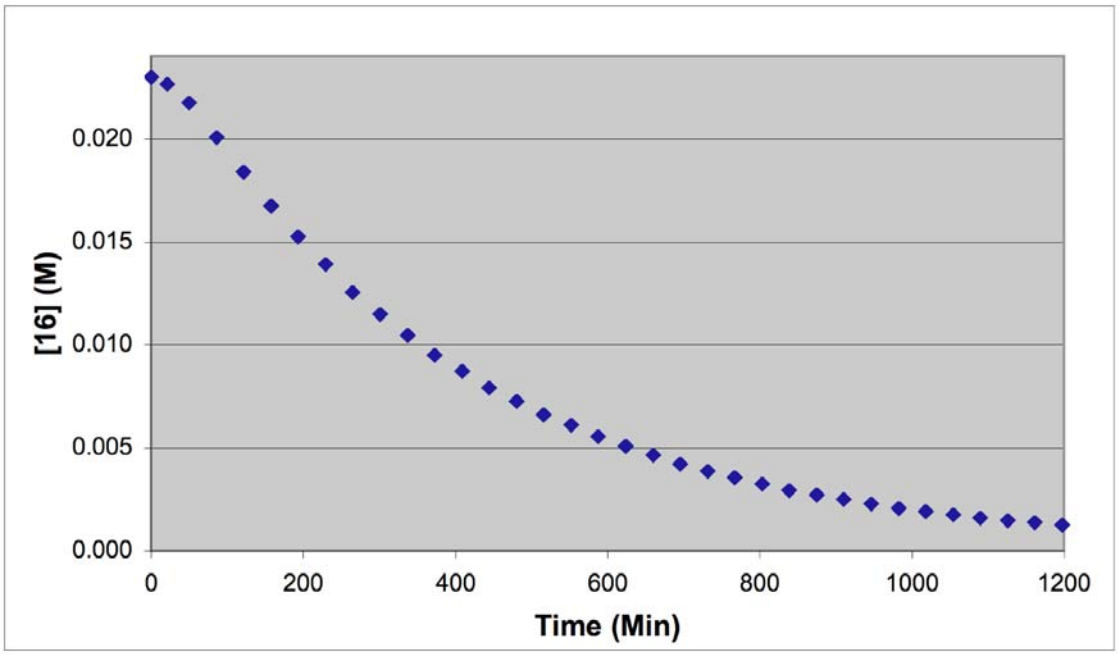


Chart S.3. Decomposition of **16**.



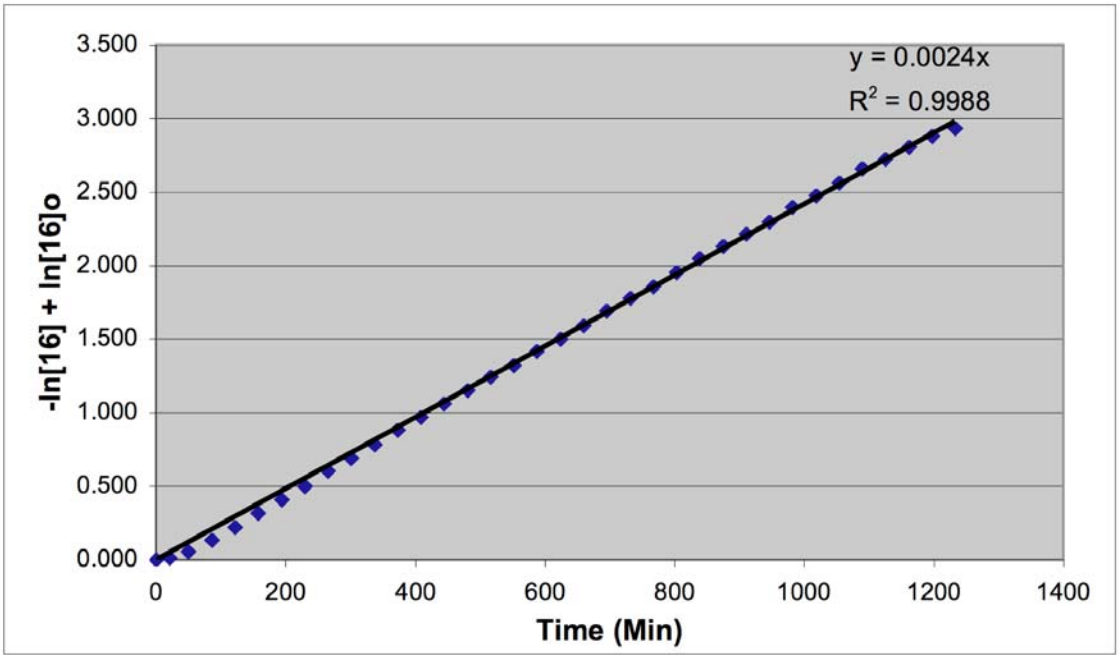
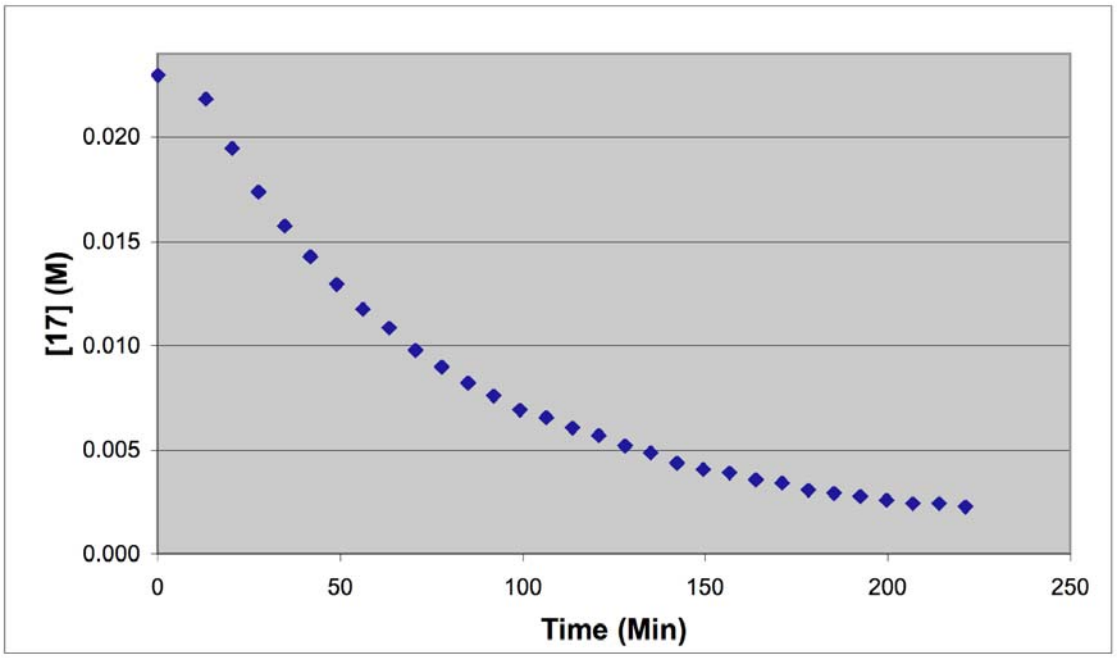


Chart S.4. Decomposition of **17**.



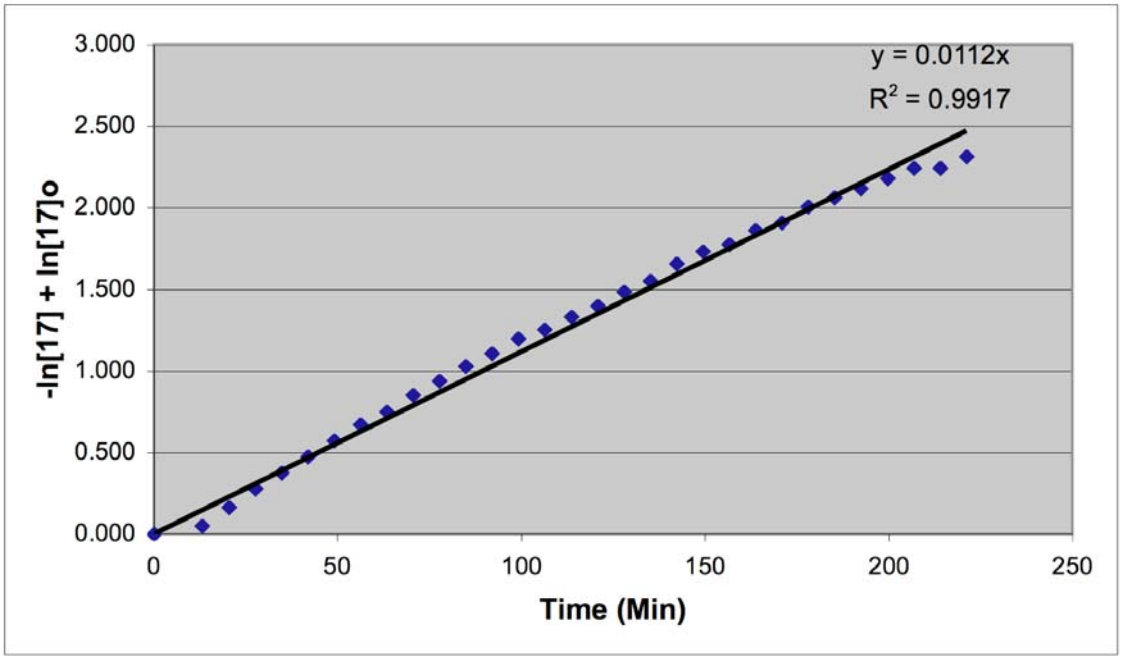


Chart S.5. Decomposition reaction of **18** with ethylene.

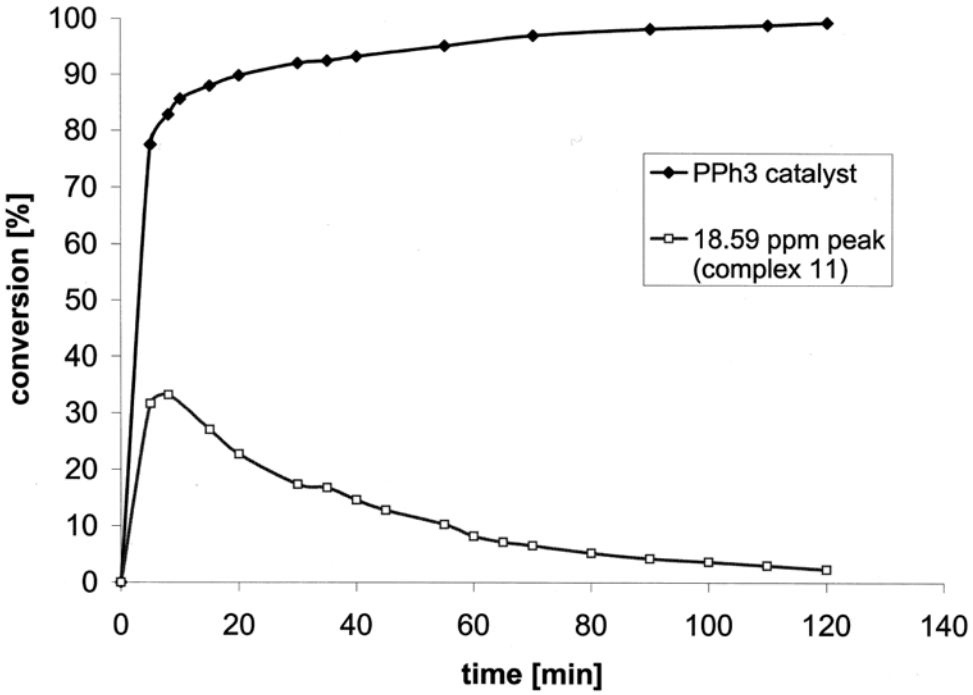


Figure S.1. ^{31}P NMR Spectrum after Decomposition of **5**.

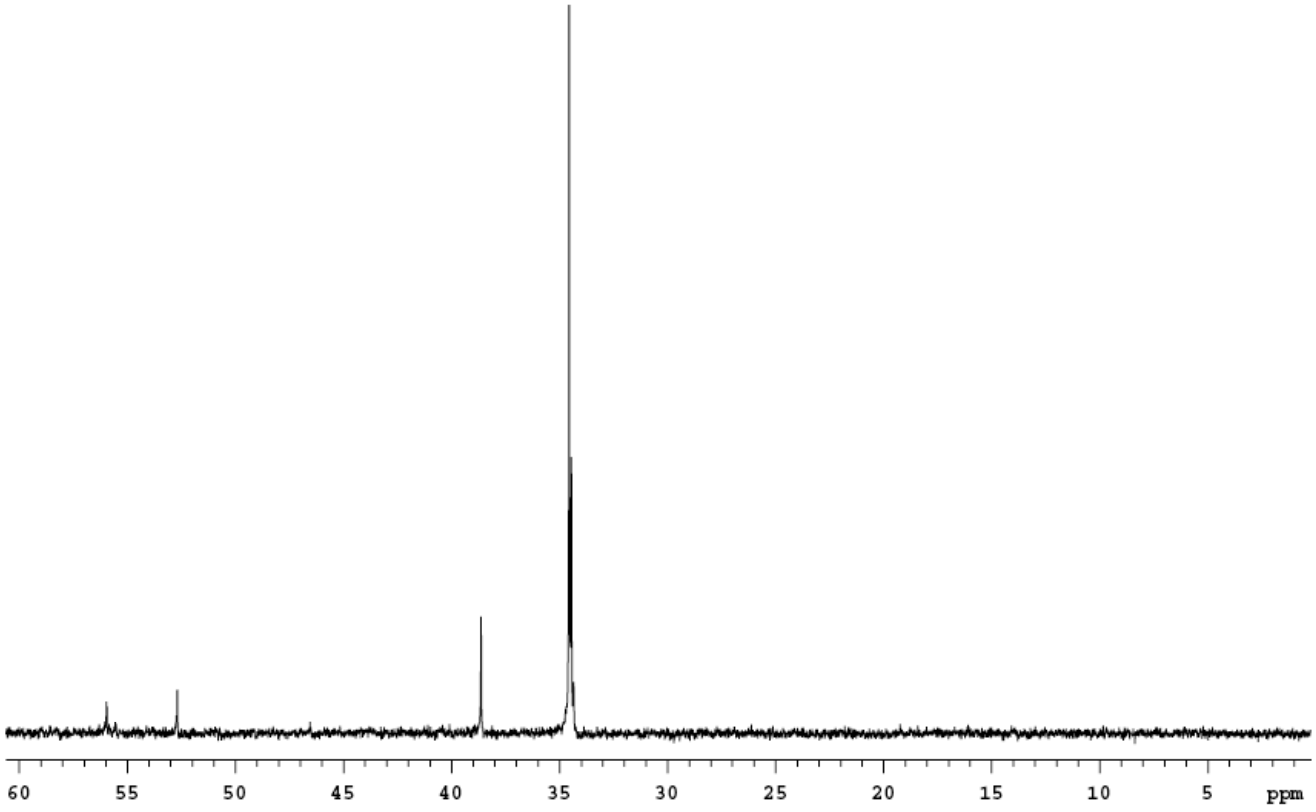


Figure S.2. ^{31}P NMR Spectrum after Decomposition of **13**.

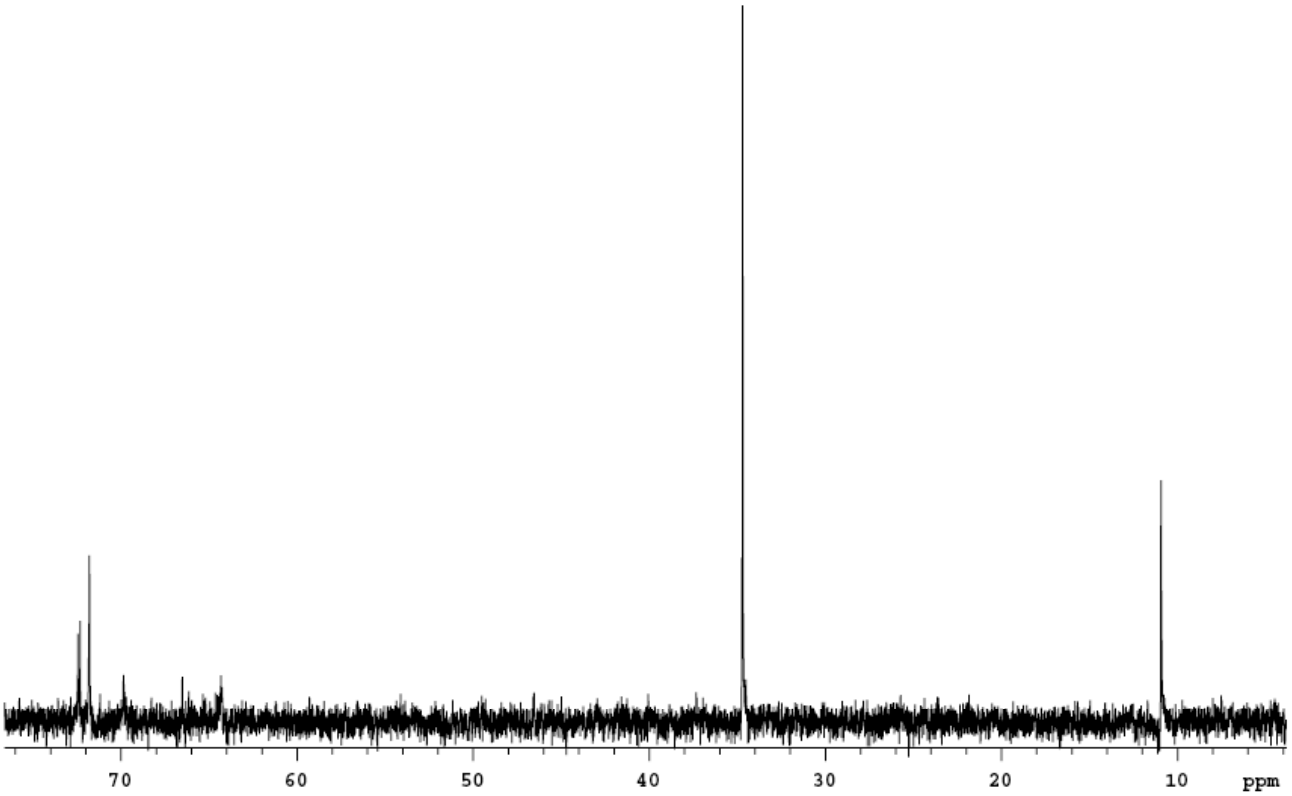


Figure S.3. ^{31}P NMR Spectrum after Decomposition of **14**.

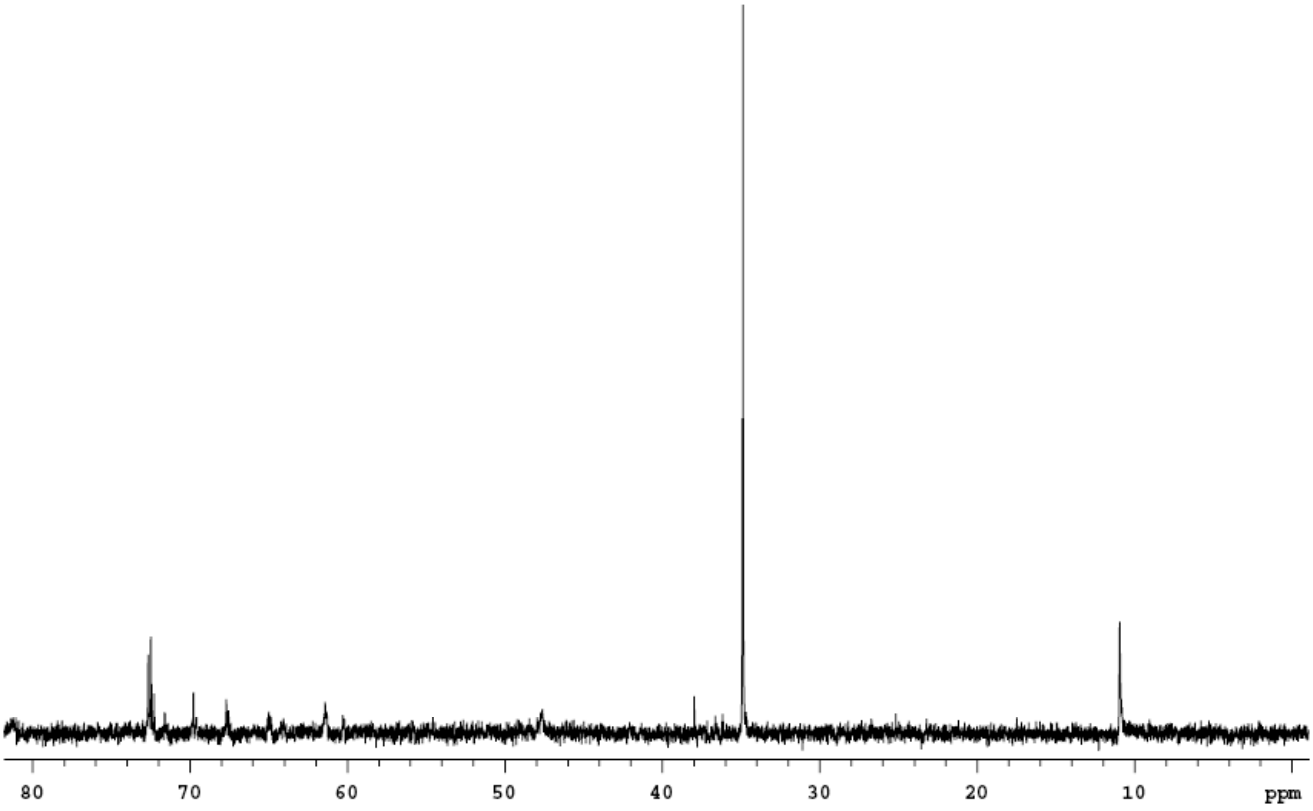


Figure S.4. ^{31}P NMR Spectrum after Decomposition of **16**.

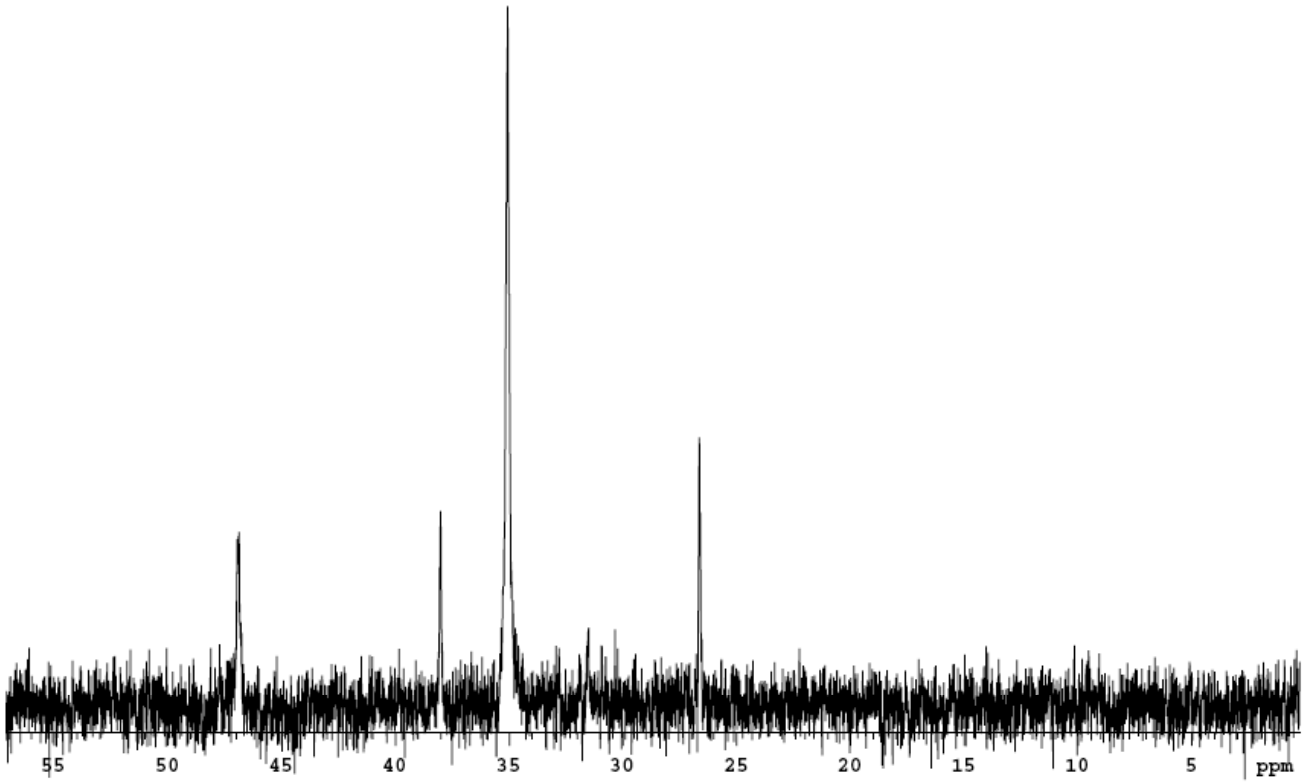


Figure S.5. ^{31}P NMR Spectrum after Decomposition of **17**.

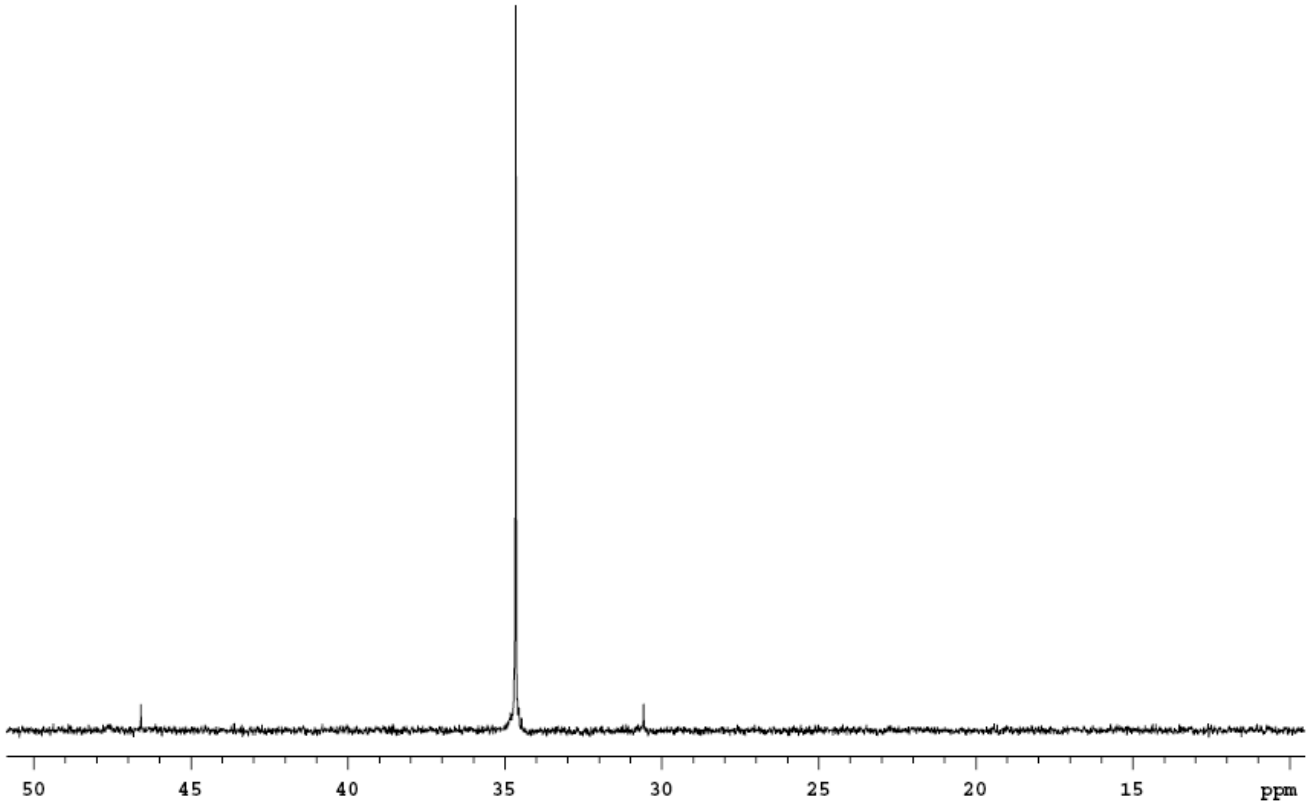


Figure S.6. Mass spectrometric analysis of the reaction of **18** with ethylene after 8 min at 23 °C.

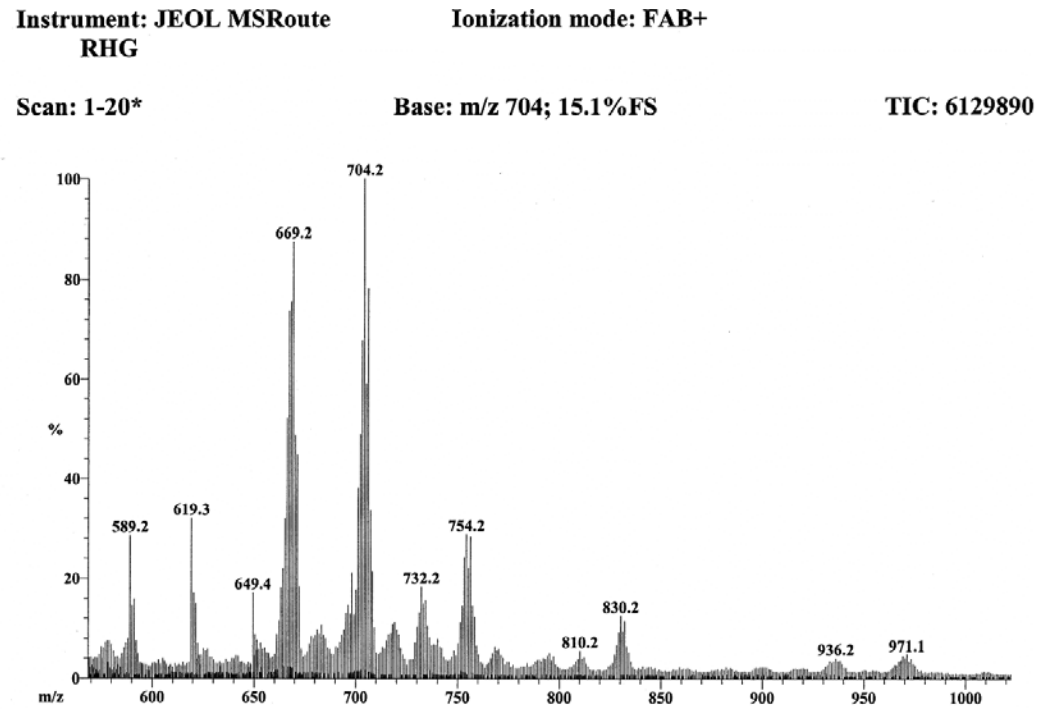
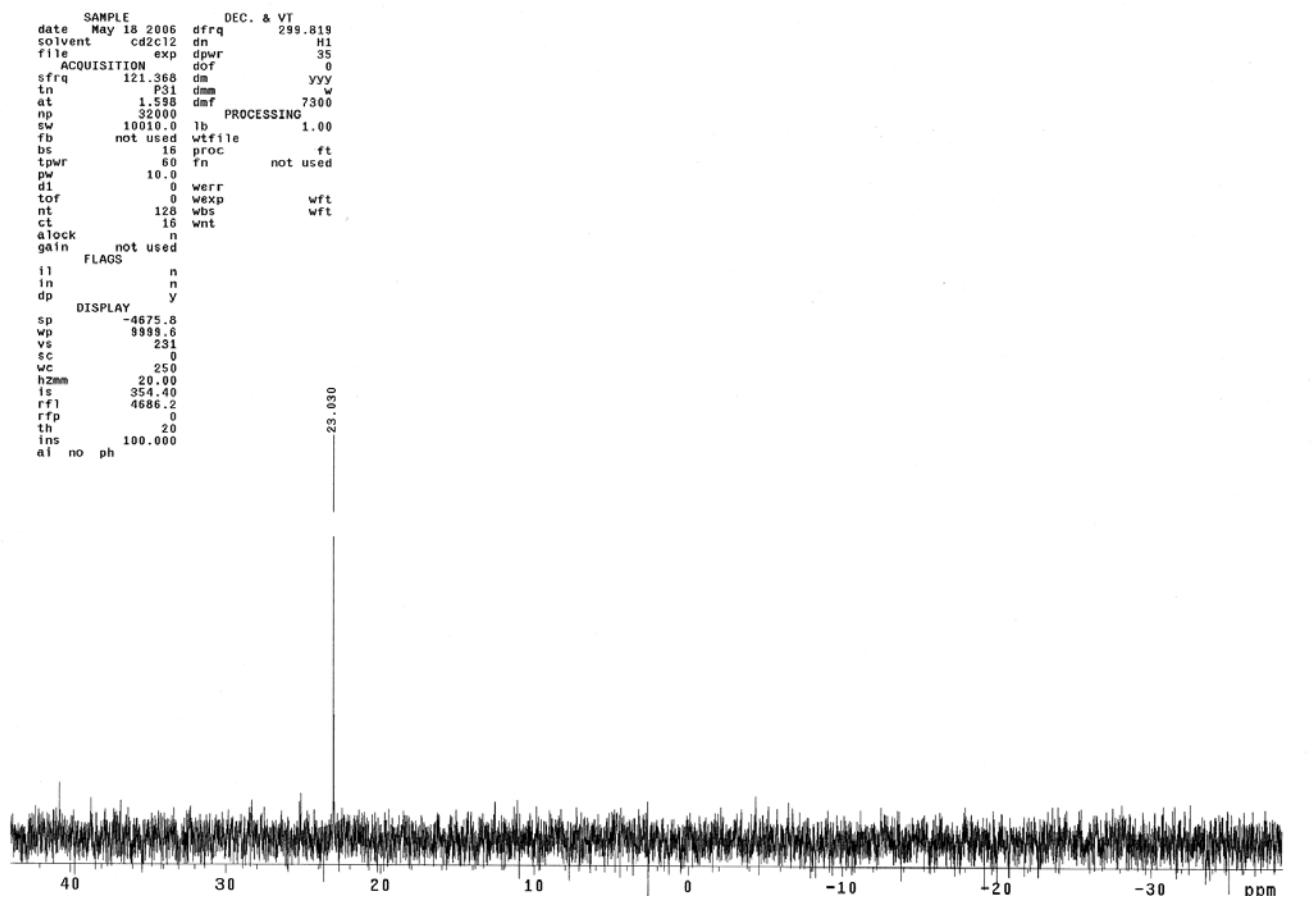
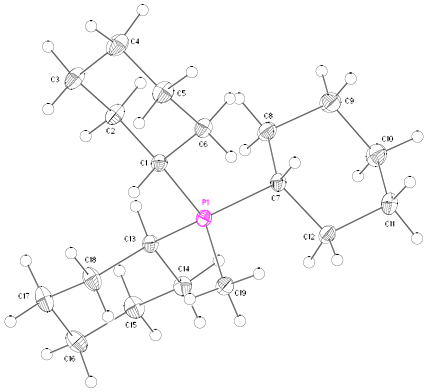


Figure S.7. ^{31}P NMR of the reaction of **18** with ethylene after 24 h.



Crystal Structure Analysis of 7

Contents



Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 288113.

Table S.1. Crystal data and structure refinement for 7 (CCDC 288113).

Empirical formula	$[C_{19}H_{36}P]^+ Cl^- \cdot 3(H_2O)$
Formula weight	384.95
Crystallization Solvent	Water
Crystal Habit	Block
Crystal size	0.30 x 0.23 x 0.18 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 8830 reflections used in lattice determination	2.47 to 35.53°	
Unit cell dimensions	a = 9.8774(4) Å b = 10.0035(5) Å c = 12.7700(6) Å	α= 85.1580(10)° β= 74.3040(10)° γ = 63.5350(10)°
Volume	1086.48(9) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.177 Mg/m^3	
F(000)	424	
Data collection program	Bruker SMART v5.630	
θ range for data collection	1.66 to 35.91°	
Completeness to θ = 35.91°	79.6 %	
Index ranges	$-15 \le h \le 16$, $-15 \le k \le 15$, $-18 \le l \le 16$	
Data collection scan type	ω scans at 5 ϕ settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	19055	
Independent reflections	8153 [R_{int}= 0.0545]	
Absorption coefficient	0.263 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9541 and 0.9252	

Table S.1 (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8153 / 0 / 361
Treatment of hydrogen atoms	Mixed
Goodness-of-fit on F^2	1.307
Final R indices [I>2σ(I), 5822 reflections]	R1 = 0.0383, *w*R2 = 0.0724
R indices (all data)	R1 = 0.0618, *w*R2 = 0.0772
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.506 and -0.365 e.Å^{-3}

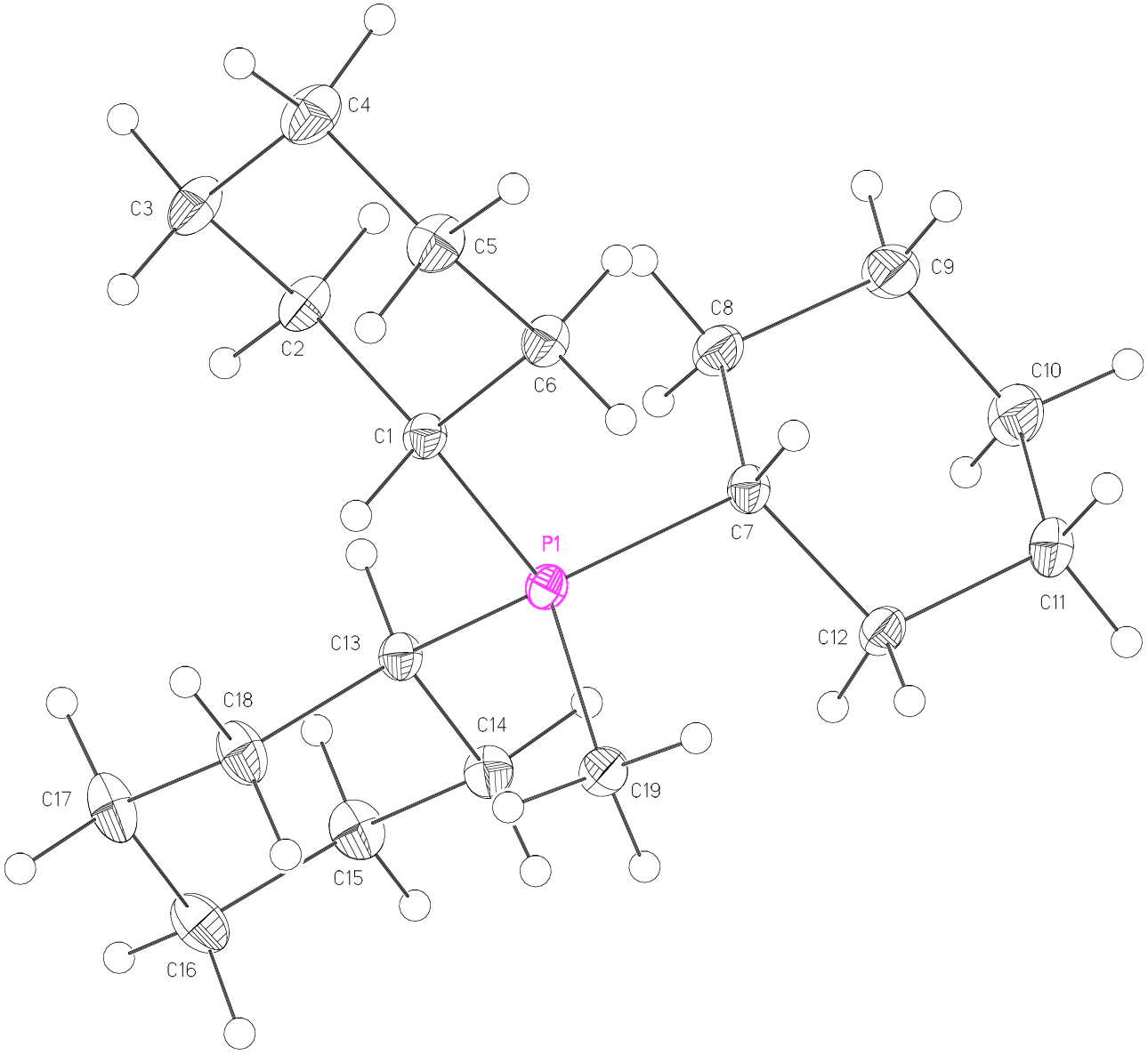
Special Refinement Details

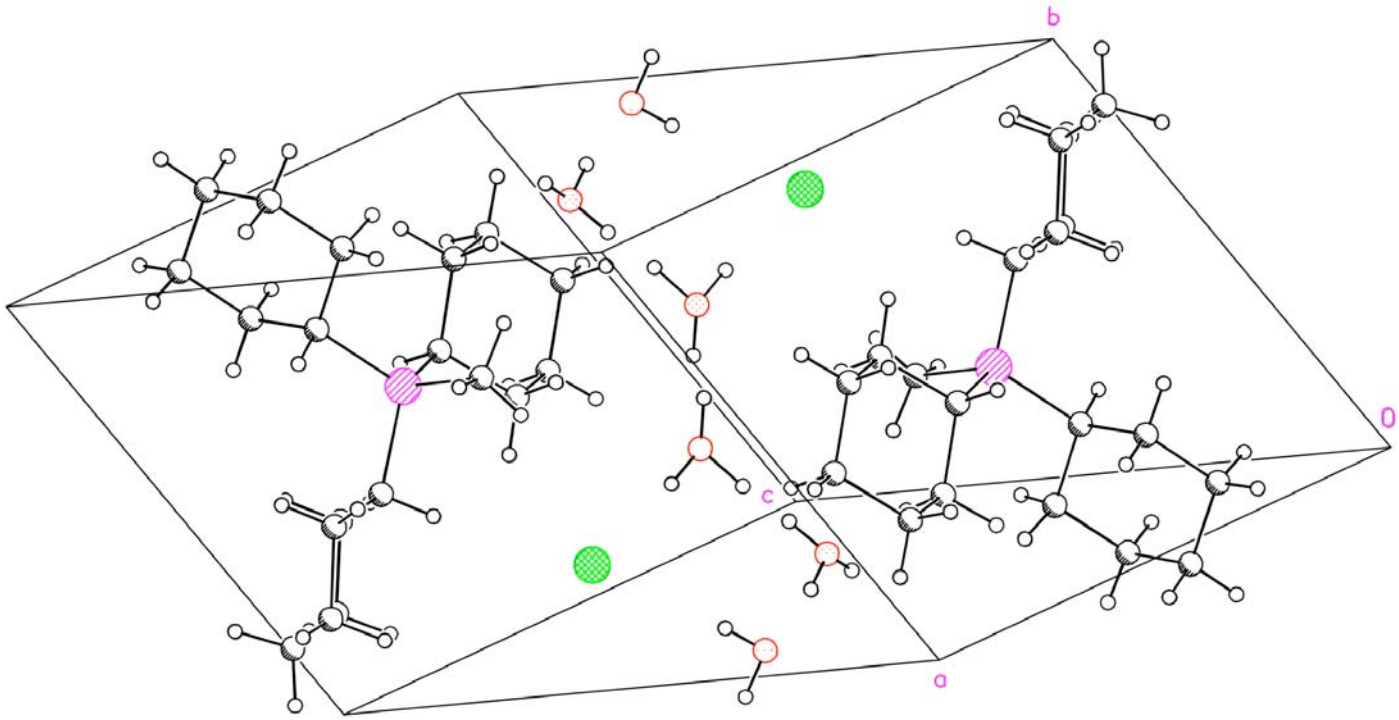
The extended structure contains a network of hydrogen bonds between water and chloride (see Table 6). The orientations of O(1) and O(3) alternate between two possible orientations in the network and therefore each have one hydrogen atom {H(1AA) and H(3AA)} in a fully occupied site; the other sites were modeled with 50:50 occupancy. Additionally, Table 6 lists donor-acceptor interactions of hydrogens bonded to C(19).

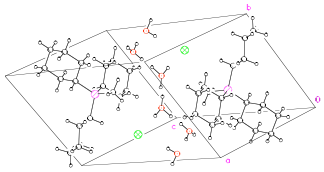
All hydrogen atoms were located in the electron difference Fourier map. Hydrogen atoms on water were restrained to ride the respective oxygen atom with the isotropic temperature factor set to 1.2 times that of the oxygen. All other hydrogen atoms were refined without restraints.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C4
C3
C5
C2
C6
C8
C9
C10
C1
C7
P1
C11
C13
C12
C18
C14
C17
C19
C15
C16


b
0
c
a



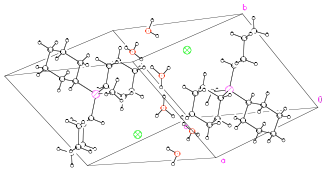


Table S.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 7 (CCDC 288113). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	843(1)	7434(1)	4983(1)	23(1)
P(1)	7499(1)	6374(1)	7287(1)	11(1)
C(1)	9079(1)	4584(1)	7476(1)	12(1)
C(2)	8913(1)	3984(1)	8628(1)	17(1)
C(3)	10209(1)	2394(1)	8609(1)	19(1)
C(4)	11836(1)	2337(1)	8142(1)	21(1)
C(5)	11995(1)	2983(1)	7018(1)	18(1)
C(6)	10698(1)	4575(1)	7041(1)	15(1)
C(7)	7758(1)	7956(1)	7647(1)	13(1)
C(8)	7413(1)	8199(1)	8878(1)	17(1)
C(9)	7652(2)	9531(1)	9144(1)	22(1)
C(10)	6667(2)	10945(1)	8629(1)	22(1)
C(11)	7072(1)	10711(1)	7403(1)	18(1)
C(12)	6845(1)	9395(1)	7094(1)	15(1)
C(13)	5645(1)	6391(1)	8075(1)	13(1)
C(14)	4202(1)	7885(1)	8081(1)	15(1)
C(15)	2691(1)	7796(1)	8726(1)	18(1)
C(16)	2525(1)	6513(1)	8300(1)	21(1)
C(17)	3952(1)	5035(1)	8306(1)	22(1)
C(18)	5457(1)	5103(1)	7643(1)	19(1)
C(19)	7583(1)	6440(1)	5871(1)	15(1)
O(1)	4337(1)	9038(1)	5373(1)	26(1)
O(2)	1175(1)	9878(1)	6256(1)	28(1)
O(3)	5521(1)	3560(1)	5392(1)	30(1)

Table S.3. Bond lengths [Å] and angles [°] for 7 (CCDC 288113).

P(1)-C(19)	1.7847(12)	C(16)-H(16A)	0.985(14)
P(1)-C(7)	1.8254(10)	C(16)-H(16B)	0.952(14)
P(1)-C(13)	1.8279(10)	C(17)-C(18)	1.5270(16)
P(1)-C(1)	1.8280(10)	C(17)-H(17A)	0.993(14)
O(1)-H(1AA)	0.8600	C(17)-H(17B)	0.934(15)
O(1)-H(1BA)	0.8444	C(18)-H(18A)	0.937(14)
O(1)-H(1BB)	0.8432	C(18)-H(18B)	0.970(13)
O(2)-H(2AA)	0.7801	C(19)-H(19A)	0.959(14)
O(2)-H(2BA)	0.8992	C(19)-H(19B)	0.978(13)
O(3)-H(3AA)	0.8799	C(19)-H(19C)	0.916(13)
O(3)-H(3BA)	0.8997		
O(3)-H(3BB)	0.9629	C(19)-P(1)-C(7)	107.73(5)
C(1)-C(2)	1.5358(16)	C(19)-P(1)-C(13)	109.74(5)
C(1)-C(6)	1.5398(14)	C(7)-P(1)-C(13)	112.79(5)
C(1)-H(1)	0.939(12)	C(19)-P(1)-C(1)	106.55(5)
C(2)-C(3)	1.5316(15)	C(7)-P(1)-C(1)	112.06(5)
C(2)-H(2A)	0.974(12)	C(13)-P(1)-C(1)	107.77(5)
C(2)-H(2B)	0.984(13)	H(1AA)-O(1)-H(1BA)	117.1
C(3)-C(4)	1.5318(16)	H(1AA)-O(1)-H(1BB)	94.4
C(3)-H(3A)	0.953(13)	H(1BA)-O(1)-H(1BB)	136.7
C(3)-H(3B)	0.963(14)	H(2AA)-O(2)-H(2BA)	100.0
C(4)-C(5)	1.5209(17)	H(3AA)-O(3)-H(3BA)	118.0
C(4)-H(4A)	1.000(14)	H(3AA)-O(3)-H(3BB)	95.0
C(4)-H(4B)	0.947(13)	H(3BA)-O(3)-H(3BB)	129.0
C(5)-C(6)	1.5320(15)	C(2)-C(1)-C(6)	110.16(9)
C(5)-H(5A)	0.966(13)	C(2)-C(1)-P(1)	116.70(7)
C(5)-H(5B)	0.947(13)	C(6)-C(1)-P(1)	111.88(7)
C(6)-H(6A)	0.926(13)	C(2)-C(1)-H(1)	108.9(8)
C(6)-H(6B)	0.948(12)	C(6)-C(1)-H(1)	107.7(8)
C(7)-C(8)	1.5323(16)	P(1)-C(1)-H(1)	100.8(7)
C(7)-C(12)	1.5485(15)	C(3)-C(2)-C(1)	109.78(9)
C(7)-H(7)	0.970(13)	C(3)-C(2)-H(2A)	108.6(7)
C(8)-C(9)	1.5309(16)	C(1)-C(2)-H(2A)	110.0(8)
C(8)-H(8A)	0.994(14)	C(3)-C(2)-H(2B)	108.5(7)
C(8)-H(8B)	0.954(13)	C(1)-C(2)-H(2B)	111.2(8)
C(9)-C(10)	1.5303(17)	H(2A)-C(2)-H(2B)	108.7(10)
C(9)-H(9A)	0.967(13)	C(2)-C(3)-C(4)	111.38(10)
C(9)-H(9B)	0.959(14)	C(2)-C(3)-H(3A)	108.0(8)
C(10)-C(11)	1.5193(17)	C(4)-C(3)-H(3A)	108.7(8)
C(10)-H(10A)	0.975(14)	C(2)-C(3)-H(3B)	109.8(7)
C(10)-H(10B)	0.986(14)	C(4)-C(3)-H(3B)	109.2(7)
C(11)-C(12)	1.5288(15)	H(3A)-C(3)-H(3B)	109.8(11)
C(11)-H(11A)	0.974(13)	C(5)-C(4)-C(3)	111.53(10)
C(11)-H(11B)	0.961(13)	C(5)-C(4)-H(4A)	109.3(8)
C(12)-H(12A)	0.927(14)	C(3)-C(4)-H(4A)	109.2(8)
C(12)-H(12B)	0.983(12)	C(5)-C(4)-H(4B)	108.7(8)
C(13)-C(14)	1.5373(14)	C(3)-C(4)-H(4B)	109.3(8)
C(13)-C(18)	1.5449(15)	H(4A)-C(4)-H(4B)	108.8(11)
C(13)-H(13)	0.931(13)	C(4)-C(5)-C(6)	111.05(9)
C(14)-C(15)	1.5339(15)	C(4)-C(5)-H(5A)	109.7(8)
C(14)-H(14A)	1.029(13)	C(6)-C(5)-H(5A)	109.2(7)
C(14)-H(14B)	0.919(14)	C(4)-C(5)-H(5B)	113.0(8)
C(15)-C(16)	1.5246(16)	C(6)-C(5)-H(5B)	108.0(7)
C(15)-H(15A)	0.967(13)	H(5A)-C(5)-H(5B)	105.8(11)
C(15)-H(15B)	0.970(14)	C(5)-C(6)-C(1)	110.04(9)
C(16)-C(17)	1.5227(17)	C(5)-C(6)-H(6A)	110.8(7)

C(1)-C(6)-H(6A)	110.6(7)
C(5)-C(6)-H(6B)	110.1(7)
C(1)-C(6)-H(6B)	109.1(7)
H(6A)-C(6)-H(6B)	106.1(10)
C(8)-C(7)-C(12)	112.57(9)
C(8)-C(7)-P(1)	112.98(7)
C(12)-C(7)-P(1)	111.83(7)
C(8)-C(7)-H(7)	110.8(8)
C(12)-C(7)-H(7)	106.9(8)
P(1)-C(7)-H(7)	101.0(8)
C(9)-C(8)-C(7)	111.29(10)
C(9)-C(8)-H(8A)	107.3(8)
C(7)-C(8)-H(8A)	111.6(8)
C(9)-C(8)-H(8B)	110.5(8)
C(7)-C(8)-H(8B)	110.5(8)
H(8A)-C(8)-H(8B)	105.6(11)
C(10)-C(9)-C(8)	111.01(10)
C(10)-C(9)-H(9A)	109.0(8)
C(8)-C(9)-H(9A)	110.1(8)
C(10)-C(9)-H(9B)	112.4(8)
C(8)-C(9)-H(9B)	109.1(8)
H(9A)-C(9)-H(9B)	105.1(11)
C(11)-C(10)-C(9)	110.89(10)
C(11)-C(10)-H(10A)	110.9(8)
C(9)-C(10)-H(10A)	109.1(8)
C(11)-C(10)-H(10B)	108.9(8)
C(9)-C(10)-H(10B)	111.1(8)
H(10A)-C(10)-H(10B)	105.8(11)
C(10)-C(11)-C(12)	111.72(9)
C(10)-C(11)-H(11A)	109.5(8)
C(12)-C(11)-H(11A)	107.5(7)
C(10)-C(11)-H(11B)	113.6(8)
C(12)-C(11)-H(11B)	106.8(7)
H(11A)-C(11)-H(11B)	107.4(11)
C(11)-C(12)-C(7)	111.27(9)
C(11)-C(12)-H(12A)	108.4(8)
C(7)-C(12)-H(12A)	109.2(8)
C(11)-C(12)-H(12B)	109.4(7)
C(7)-C(12)-H(12B)	110.7(7)
H(12A)-C(12)-H(12B)	107.8(11)
C(14)-C(13)-C(18)	110.40(9)
C(14)-C(13)-P(1)	114.13(7)
C(18)-C(13)-P(1)	109.12(7)
C(14)-C(13)-H(13)	107.9(7)
C(18)-C(13)-H(13)	108.6(7)
P(1)-C(13)-H(13)	106.5(7)
C(15)-C(14)-C(13)	111.06(9)
C(15)-C(14)-H(14A)	108.1(7)
C(13)-C(14)-H(14A)	110.1(7)
C(15)-C(14)-H(14B)	108.2(8)
C(13)-C(14)-H(14B)	110.4(8)
H(14A)-C(14)-H(14B)	109.0(10)
C(16)-C(15)-C(14)	111.79(9)
C(16)-C(15)-H(15A)	110.5(7)
C(14)-C(15)-H(15A)	109.2(7)
C(16)-C(15)-H(15B)	109.3(7)
C(14)-C(15)-H(15B)	111.0(7)
H(15A)-C(15)-H(15B)	104.8(10)
C(17)-C(16)-C(15)	110.84(9)
C(17)-C(16)-H(16A)	109.7(7)
C(15)-C(16)-H(16A)	108.9(7)
C(17)-C(16)-H(16B)	111.0(8)
C(15)-C(16)-H(16B)	110.9(8)
H(16A)-C(16)-H(16B)	105.3(11)
C(16)-C(17)-C(18)	111.11(10)
C(16)-C(17)-H(17A)	108.9(7)
C(18)-C(17)-H(17A)	110.6(7)
C(16)-C(17)-H(17B)	109.9(9)
C(18)-C(17)-H(17B)	108.8(9)
H(17A)-C(17)-H(17B)	107.4(12)
C(17)-C(18)-C(13)	111.06(9)
C(17)-C(18)-H(18A)	108.4(8)
C(13)-C(18)-H(18A)	106.3(8)
C(17)-C(18)-H(18B)	111.1(8)
C(13)-C(18)-H(18B)	111.3(7)
H(18A)-C(18)-H(18B)	108.4(11)
P(1)-C(19)-H(19A)	108.8(8)
P(1)-C(19)-H(19B)	109.2(8)
H(19A)-C(19)-H(19B)	108.8(11)
P(1)-C(19)-H(19C)	109.6(8)
H(19A)-C(19)-H(19C)	110.1(11)
H(19B)-C(19)-H(19C)	110.3(11)

Table S.4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 7 (CCDC 288113). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	205(1)	166(1)	314(2)	-3(1)	-21(1)	-98(1)
P(1)	113(1)	96(1)	116(1)	4(1)	-27(1)	-39(1)
C(1)	129(4)	98(5)	136(6)	4(4)	-38(4)	-40(4)
C(2)	156(5)	149(5)	150(6)	36(4)	-25(4)	-43(4)
C(3)	164(5)	165(5)	194(7)	64(4)	-37(5)	-41(4)
C(4)	147(5)	182(6)	237(7)	50(5)	-46(5)	-23(4)
C(5)	121(4)	167(5)	199(7)	10(4)	-15(4)	-25(4)
C(6)	134(4)	140(5)	146(6)	15(4)	-21(4)	-53(4)
C(7)	129(4)	106(5)	143(6)	5(4)	-28(4)	-50(4)
C(8)	232(5)	143(5)	143(6)	18(4)	-72(5)	-78(4)
C(9)	322(6)	170(6)	207(7)	7(4)	-130(5)	-106(5)
C(10)	293(6)	126(5)	221(7)	-14(4)	-85(5)	-71(5)
C(11)	204(5)	129(5)	206(6)	26(4)	-47(5)	-82(4)
C(12)	187(5)	136(5)	126(6)	26(4)	-48(4)	-71(4)
C(13)	127(4)	112(5)	135(6)	2(4)	-27(4)	-52(4)
C(14)	122(4)	128(5)	180(6)	0(4)	-27(4)	-40(4)
C(15)	133(4)	175(5)	207(7)	-29(4)	-6(4)	-57(4)
C(16)	153(5)	244(6)	243(7)	-24(5)	-29(5)	-112(4)
C(17)	202(5)	179(6)	290(8)	-34(5)	-19(5)	-118(5)
C(18)	165(5)	147(5)	249(7)	-45(4)	-18(5)	-75(4)
C(19)	164(5)	135(5)	134(6)	1(4)	-38(4)	-58(4)
O(1)	188(4)	217(4)	380(6)	48(4)	-88(4)	-91(3)
O(2)	229(4)	230(4)	388(6)	-45(4)	-84(4)	-86(4)
O(3)	214(4)	255(5)	403(6)	-48(4)	-102(4)	-60(4)

Table S.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 7 (CCDC 288113).

	x	y	z	U_{iso}
H(1AA)	3337	9429	5636	31
H(1BA)	4742	9629	5146	31
H(1BB)	4396	8244	5142	31
H(2AA)	1078	9245	6014	34
H(2BA)	592	10666	5920	34
H(3AA)	6537	3222	5299	36
H(3BA)	4983	4502	5208	36
H(3BB)	5590	2644	5145	36
H(1)	9011(14)	3950(13)	7011(10)	18(3)
H(2A)	9006(14)	4616(13)	9118(10)	17(3)
H(2B)	7892(15)	3963(13)	8913(10)	20(3)
H(3A)	10077(15)	1774(14)	8158(11)	21(3)
H(3B)	10131(14)	2034(13)	9336(11)	19(3)
H(4A)	12021(15)	2916(14)	8645(12)	24(3)
H(4B)	12606(15)	1330(15)	8087(11)	25(3)
H(5A)	11936(15)	2360(14)	6510(11)	21(3)
H(5B)	12971(15)	3011(13)	6731(10)	19(3)
H(6A)	10795(13)	4962(13)	6355(11)	12(3)
H(6B)	10789(13)	5215(13)	7495(10)	15(3)
H(7)	8862(15)	7638(14)	7299(11)	24(3)
H(8A)	6313(16)	8405(15)	9255(12)	30(4)
H(8B)	8052(15)	7317(15)	9184(11)	24(3)
H(9A)	8744(16)	9320(14)	8876(11)	23(3)
H(9B)	7420(14)	9654(14)	9918(12)	21(3)
H(10A)	5560(16)	11220(15)	8956(11)	28(4)
H(10B)	6833(15)	11800(15)	8790(11)	26(4)
H(11A)	8167(15)	10492(14)	7089(11)	23(3)
H(11B)	6456(14)	11564(14)	7049(11)	19(3)
H(12A)	7208(14)	9232(14)	6345(11)	20(3)
H(12B)	5722(14)	9651(13)	7297(10)	16(3)
H(13)	5719(14)	6211(13)	8789(11)	14(3)
H(14A)	4284(14)	8721(14)	8438(11)	20(3)
H(14B)	4127(14)	8131(14)	7382(11)	18(3)
H(15A)	1803(15)	8737(14)	8693(11)	21(3)
H(15B)	2651(14)	7683(13)	9494(11)	16(3)
H(16A)	2410(15)	6711(14)	7553(12)	21(3)
H(16B)	1587(16)	6467(15)	8711(12)	30(4)
H(17A)	3992(14)	4795(13)	9070(11)	19(3)
H(17B)	3859(16)	4267(16)	8009(12)	37(4)
H(18A)	5385(14)	5321(14)	6927(11)	19(3)
H(18B)	6364(15)	4153(14)	7630(11)	21(3)
H(19A)	8459(15)	6619(14)	5481(11)	24(3)
H(19B)	6622(16)	7263(15)	5758(11)	26(4)
H(19C)	7691(15)	5551(14)	5631(11)	21(3)

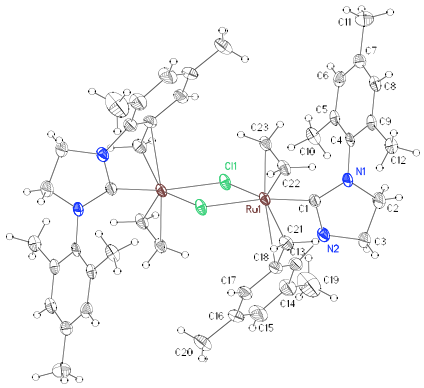
Table S.6. Hydrogen bonds for 7 (CCDC 288113) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1AA)...O(2)	0.86	1.92	2.7656(11)	168.1
O(1)-H(1BA)...O(1)#1	0.84	1.91	2.7553(16)	179.8
O(1)-H(1BB)...O(3)#2	0.84	1.94	2.7856(12)	178.6
O(2)-H(2AA)...Cl(1)	0.78	2.45	3.2242(9)	171.1
O(2)-H(2BA)...Cl(1)#3	0.90	2.25	3.1494(10)	177.4
O(3)-H(3AA)...Cl(1)#2	0.88	2.30	3.1747(9)	174.6
O(3)-H(3BA)...O(3)#2	0.90	1.92	2.7914(18)	162.3
O(3)-H(3BB)...O(1)#2	0.96	1.82	2.7856(12)	177.1
Other Hydrogen Donor-Acceptor Interactions				
C(19)-H(19A)...Cl(1)#4	0.959(14)	2.726(14)	3.6522(12)	162.5(11)
C(19)-H(19B)...O(1)	0.978(13)	2.317(14)	3.2919(14)	174.0(11)
C(19)-H(19C)...Cl(1)#2	0.916(13)	2.749(13)	3.6128(12)	157.6(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1
#2 -x+1,-y+1,-z+1
#3 -x,-y+2,-z+1
#4 x+1, y, z

Crystal Structure Analysis of 21

Contents



Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 612720.

Table S.8. Crystal data and structure refinement for 21 (CCDC 612720).

Empirical formula	$C_{46}H_{58}N_4Cl_2Ru_2$
Formula weight	940.00
Crystallization Solvent	Toluene/pentane
Crystal Habit	Plate
Crystal size	0.21 x 0.18 x 0.07 mm^3
Crystal color	Dichroic - Red/brown

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 8556 reflections used in lattice determination	2.21 to 33.51°	
Unit cell dimensions	a = 9.8735(6) Å b = 10.7053(7) Å c = 11.8315(7) Å	α= 100.828(2)° β= 98.018(2)° γ = 116.4470(10)°
Volume	1063.77(11) $Å^3$	
Z	1	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.467 Mg/m^3	
F(000)	484	
Data collection program	Bruker SMART v5.630	
θ range for data collection	1.81 to 34.93°	
Completeness to θ = 34.93°	84.1 %	
Index ranges	$-15 \le h \le 15$, $-13 \le k \le 16$, $-18 \le l \le 18$	
Data collection scan type	ω scans at 6 ϕ settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	19483	
Independent reflections	7835 [R_{int}= 0.0644]	
Absorption coefficient	0.872 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9415 and 0.8380	

Table S.8. (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	7835 / 0 / 360
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.146
Final R indices [I>2σ(I), 5514 reflections]	R1 = 0.0422, *w*R2 = 0.0667
R indices (all data)	R1 = 0.0724, *w*R2 = 0.0714
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	1.257 and -1.008 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

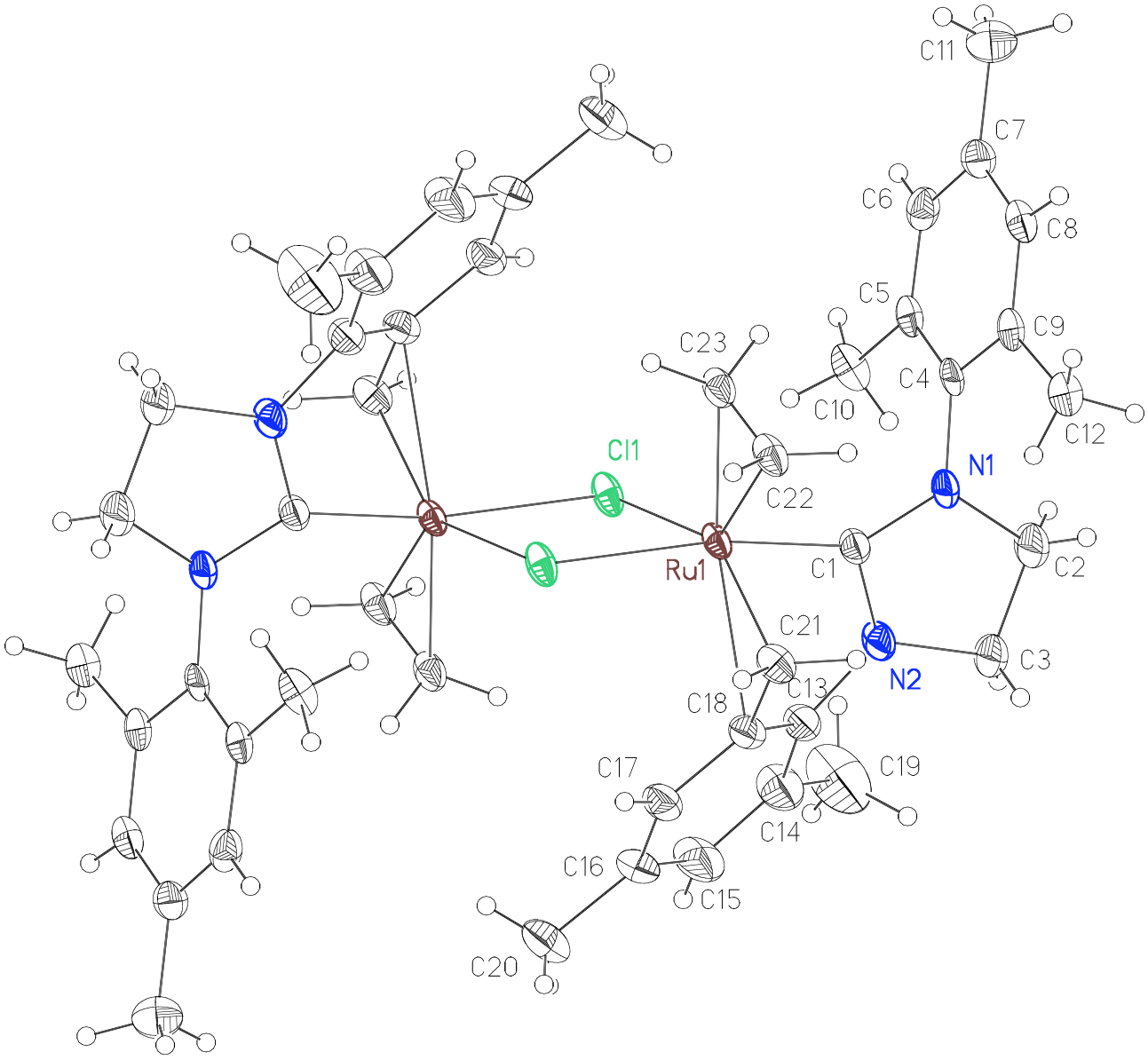

C11
C7
C6
C8
C5
C9
C23
C4
C10
C12
Cl1
N1
C22
Ru1
C1
C2
C21
N2
C3
C18
C13
C17
C19
C14
C16
C15
C20

Table S.9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 21 (CCDC 612720). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	5580(1)	6883(1)	5879(1)	18(1)
Cl(1)	3635(1)	4368(1)	5729(1)	22(1)
N(1)	5407(2)	8846(2)	8079(2)	23(1)
N(2)	3784(2)	8212(2)	6359(2)	26(1)
C(1)	4919(2)	7991(2)	6930(2)	20(1)
C(2)	4490(4)	9596(4)	8297(2)	41(1)
C(3)	3580(4)	9368(3)	7075(2)	32(1)
C(4)	6160(3)	8616(3)	9083(2)	21(1)
C(5)	5372(3)	7352(2)	9424(2)	22(1)
C(6)	6097(3)	7212(3)	10440(2)	26(1)
C(7)	7571(3)	8289(3)	11145(2)	25(1)
C(8)	8293(3)	9536(3)	10795(2)	24(1)
C(9)	7632(3)	9748(3)	9789(2)	22(1)
C(10)	3759(3)	6167(3)	8701(2)	31(1)
C(11)	8331(4)	8104(4)	12243(3)	36(1)
C(12)	8429(3)	11170(3)	9504(2)	28(1)
C(13)	3288(3)	7659(3)	5089(2)	26(1)
C(14)	1697(3)	6957(3)	4507(2)	39(1)
C(15)	1288(3)	6341(4)	3282(2)	42(1)
C(16)	2360(3)	6342(3)	2644(2)	33(1)
C(17)	3906(3)	7047(3)	3241(2)	28(1)
C(18)	4427(3)	7775(3)	4464(2)	24(1)
C(19)	482(4)	6844(6)	5159(4)	69(1)
C(20)	1827(4)	5558(4)	1328(2)	45(1)
C(21)	6105(3)	8574(3)	5118(2)	25(1)
C(22)	7925(3)	8196(3)	6807(2)	26(1)
C(23)	7314(3)	6891(3)	7123(2)	26(1)

Table S.10. Selected bond lengths [Å] and angles [°] for 21 (CCDC 612720).

Ru(1)-C(1)	1.935(2)	C(1)-Ru(1)-C(21)	82.08(10)
Ru(1)-C(21)	2.065(3)	C(1)-Ru(1)-C(22)	92.40(9)
Ru(1)-C(22)	2.086(2)	C(21)-Ru(1)-C(22)	81.43(10)
Ru(1)-C(23)	2.091(2)	C(1)-Ru(1)-C(23)	99.58(9)
Ru(1)-Cl(1)	2.4671(6)	C(21)-Ru(1)-C(23)	120.55(10)
Ru(1)-Cl(1)#1	2.5289(5)	C(22)-Ru(1)-C(23)	39.21(10)
Cl(1)-Ru(1)#1	2.5290(5)	C(1)-Ru(1)-Cl(1)	101.39(7)
		C(21)-Ru(1)-Cl(1)	144.76(6)
		C(22)-Ru(1)-Cl(1)	132.79(8)
		C(23)-Ru(1)-Cl(1)	93.71(8)
		C(1)-Ru(1)-Cl(1)#1	170.94(7)
		C(21)-Ru(1)-Cl(1)#1	89.68(7)
		C(22)-Ru(1)-Cl(1)#1	90.07(6)
		C(23)-Ru(1)-Cl(1)#1	87.82(6)
		Cl(1)-Ru(1)-Cl(1)#1	83.190(19)
		Ru(1)-Cl(1)-Ru(1)#1	96.809(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S.11. Bond lengths [Å] and angles [°] for 21 (CCDC 612720).

Ru(1)-C(1)	1.935(2)	C(21)-H(21B)	0.88(3)
Ru(1)-C(21)	2.065(3)	C(22)-C(23)	1.402(4)
Ru(1)-C(22)	2.086(2)	C(22)-H(22A)	0.99(2)
Ru(1)-C(23)	2.091(2)	C(22)-H(22B)	0.99(3)
Ru(1)-Cl(1)	2.4671(6)	C(23)-H(23A)	1.00(3)
Ru(1)-Cl(1)#1	2.5289(5)	C(23)-H(23B)	0.94(2)
Cl(1)-Ru(1)#1	2.5290(5)		
N(1)-C(1)	1.369(2)	C(1)-Ru(1)-C(21)	82.08(10)
N(1)-C(4)	1.432(3)	C(1)-Ru(1)-C(22)	92.40(9)
N(1)-C(2)	1.471(3)	C(21)-Ru(1)-C(22)	81.43(10)
N(2)-C(1)	1.361(3)	C(1)-Ru(1)-C(23)	99.58(9)
N(2)-C(13)	1.432(3)	C(21)-Ru(1)-C(23)	120.55(10)
N(2)-C(3)	1.470(3)	C(22)-Ru(1)-C(23)	39.21(10)
C(2)-C(3)	1.506(4)	C(1)-Ru(1)-Cl(1)	101.39(7)
C(2)-H(2A)	0.88(3)	C(21)-Ru(1)-Cl(1)	144.76(6)
C(2)-H(2B)	0.94(4)	C(22)-Ru(1)-Cl(1)	132.79(8)
C(3)-H(3A)	0.88(3)	C(23)-Ru(1)-Cl(1)	93.71(8)
C(3)-H(3B)	1.02(3)	C(1)-Ru(1)-Cl(1)#1	170.94(7)
C(4)-C(5)	1.398(3)	C(21)-Ru(1)-Cl(1)#1	89.68(7)
C(4)-C(9)	1.411(3)	C(22)-Ru(1)-Cl(1)#1	90.07(6)
C(5)-C(6)	1.380(3)	C(23)-Ru(1)-Cl(1)#1	87.82(6)
C(5)-C(10)	1.513(3)	Cl(1)-Ru(1)-Cl(1)#1	83.190(19)
C(6)-C(7)	1.396(3)	Ru(1)-Cl(1)-Ru(1)#1	96.809(19)
C(6)-H(6)	0.82(2)	C(1)-N(1)-C(4)	125.42(18)
C(7)-C(8)	1.379(3)	C(1)-N(1)-C(2)	111.87(19)
C(7)-C(11)	1.499(4)	C(4)-N(1)-C(2)	117.47(17)
C(8)-C(9)	1.383(3)	C(1)-N(2)-C(13)	117.14(17)
C(8)-H(8)	0.85(2)	C(1)-N(2)-C(3)	114.08(18)
C(9)-C(12)	1.500(4)	C(13)-N(2)-C(3)	125.8(2)
C(10)-H(10A)	0.93(3)	N(2)-C(1)-N(1)	106.28(18)
C(10)-H(10B)	0.91(3)	N(2)-C(1)-Ru(1)	113.79(14)
C(10)-H(10C)	0.99(3)	N(1)-C(1)-Ru(1)	138.88(16)
C(11)-H(11A)	0.91(3)	N(1)-C(2)-C(3)	104.26(19)
C(11)-H(11B)	0.99(3)	N(1)-C(2)-H(2A)	105.9(18)
C(11)-H(11C)	0.89(3)	C(3)-C(2)-H(2A)	116.6(19)
C(12)-H(12A)	0.96(3)	N(1)-C(2)-H(2B)	109(2)
C(12)-H(12B)	0.90(2)	C(3)-C(2)-H(2B)	115(2)
C(12)-H(12C)	0.89(3)	H(2A)-C(2)-H(2B)	106(3)
C(13)-C(14)	1.400(3)	N(2)-C(3)-C(2)	101.3(2)
C(13)-C(18)	1.403(3)	N(2)-C(3)-H(3A)	109(2)
C(14)-C(15)	1.392(3)	C(2)-C(3)-H(3A)	114(2)
C(14)-C(19)	1.487(4)	N(2)-C(3)-H(3B)	106.7(14)
C(15)-C(16)	1.383(4)	C(2)-C(3)-H(3B)	106.2(14)
C(15)-H(15)	0.86(3)	H(3A)-C(3)-H(3B)	119(3)
C(16)-C(17)	1.368(3)	C(5)-C(4)-C(9)	120.7(2)
C(16)-C(20)	1.514(3)	C(5)-C(4)-N(1)	120.10(19)
C(17)-C(18)	1.406(3)	C(9)-C(4)-N(1)	118.8(2)
C(17)-H(17)	0.84(2)	C(6)-C(5)-C(4)	118.4(2)
C(18)-C(21)	1.485(3)	C(6)-C(5)-C(10)	120.7(2)
C(19)-H(19A)	0.98(3)	C(4)-C(5)-C(10)	120.9(2)
C(19)-H(19B)	0.96(4)	C(5)-C(6)-C(7)	122.6(2)
C(19)-H(19C)	1.00(4)	C(5)-C(6)-H(6)	118.5(17)
C(20)-H(20A)	0.89(4)	C(7)-C(6)-H(6)	118.9(17)
C(20)-H(20B)	0.89(4)	C(8)-C(7)-C(6)	117.3(2)
C(20)-H(20C)	1.03(4)	C(8)-C(7)-C(11)	121.4(2)
C(21)-H(21A)	1.07(3)	C(6)-C(7)-C(11)	121.4(2)

C(7)-C(8)-C(9)	123.1(2)
C(7)-C(8)-H(8)	121.7(17)
C(9)-C(8)-H(8)	115.1(17)
C(8)-C(9)-C(4)	117.8(2)
C(8)-C(9)-C(12)	120.5(2)
C(4)-C(9)-C(12)	121.6(2)
C(5)-C(10)-H(10A)	108.8(15)
C(5)-C(10)-H(10B)	109.9(16)
H(10A)-C(10)-H(10B)	105(2)
C(5)-C(10)-H(10C)	111.9(14)
H(10A)-C(10)-H(10C)	114(2)
H(10B)-C(10)-H(10C)	107(2)
C(7)-C(11)-H(11A)	111.0(19)
C(7)-C(11)-H(11B)	110.3(19)
H(11A)-C(11)-H(11B)	108(3)
C(7)-C(11)-H(11C)	107(2)
H(11A)-C(11)-H(11C)	110(3)
H(11B)-C(11)-H(11C)	111(3)
C(9)-C(12)-H(12A)	111.1(17)
C(9)-C(12)-H(12B)	113.0(16)
H(12A)-C(12)-H(12B)	105(2)
C(9)-C(12)-H(12C)	111.4(19)
H(12A)-C(12)-H(12C)	107(2)
H(12B)-C(12)-H(12C)	109(2)
C(14)-C(13)-C(18)	121.6(2)
C(14)-C(13)-N(2)	120.1(2)
C(18)-C(13)-N(2)	118.20(19)
C(15)-C(14)-C(13)	117.0(2)
C(15)-C(14)-C(19)	120.9(3)
C(13)-C(14)-C(19)	122.1(2)
C(16)-C(15)-C(14)	123.2(2)
C(16)-C(15)-H(15)	118.0(16)
C(14)-C(15)-H(15)	118.6(16)
C(17)-C(16)-C(15)	118.1(2)
C(17)-C(16)-C(20)	121.2(3)
C(15)-C(16)-C(20)	120.7(3)
C(16)-C(17)-C(18)	122.3(2)
C(16)-C(17)-H(17)	120.1(17)
C(18)-C(17)-H(17)	117.5(17)
C(13)-C(18)-C(17)	117.5(2)
C(13)-C(18)-C(21)	119.49(19)
C(17)-C(18)-C(21)	122.9(2)
C(14)-C(19)-H(19A)	108.4(18)
C(14)-C(19)-H(19B)	118.9(19)
H(19A)-C(19)-H(19B)	101(3)
C(14)-C(19)-H(19C)	111(2)
H(19A)-C(19)-H(19C)	119(3)
H(19B)-C(19)-H(19C)	99(3)
C(16)-C(20)-H(20A)	109(3)
C(16)-C(20)-H(20B)	110(2)
H(20A)-C(20)-H(20B)	106(3)
C(16)-C(20)-H(20C)	113(2)
H(20A)-C(20)-H(20C)	108(3)
H(20B)-C(20)-H(20C)	110(3)
C(18)-C(21)-Ru(1)	86.08(15)
C(18)-C(21)-H(21A)	119.9(13)
Ru(1)-C(21)-H(21A)	118.2(13)
C(18)-C(21)-H(21B)	112.9(19)
Ru(1)-C(21)-H(21B)	116(2)
H(21A)-C(21)-H(21B)	104(2)
C(23)-C(22)-Ru(1)	70.58(13)
C(23)-C(22)-H(22A)	116.7(15)
Ru(1)-C(22)-H(22A)	112.9(14)
C(23)-C(22)-H(22B)	121.8(16)
Ru(1)-C(22)-H(22B)	116.4(15)
H(22A)-C(22)-H(22B)	112(2)
C(22)-C(23)-Ru(1)	70.20(13)
C(22)-C(23)-H(23A)	120.7(16)
Ru(1)-C(23)-H(23A)	117.0(15)
C(22)-C(23)-H(23B)	120.0(13)
Ru(1)-C(23)-H(23B)	112.3(12)
H(23A)-C(23)-H(23B)	111(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1.

Table S.12. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 21 (CCDC 612720). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

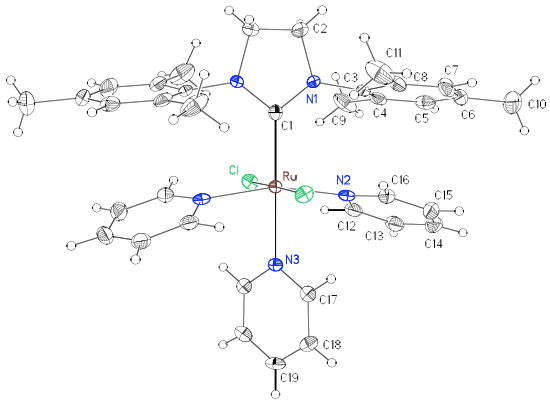
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	155(1)	234(1)	127(1)	-15(1)	28(1)	100(1)
Cl(1)	175(2)	255(3)	185(2)	-19(2)	70(2)	85(2)
N(1)	290(10)	248(11)	165(8)	-4(8)	57(7)	177(9)
N(2)	267(10)	370(12)	188(9)	-7(8)	39(7)	232(10)
C(1)	216(11)	219(13)	168(10)	15(9)	41(8)	115(10)
C(2)	570(19)	540(20)	264(13)	-10(14)	68(13)	450(18)
C(3)	393(16)	373(17)	267(12)	29(11)	94(11)	280(14)
C(4)	286(12)	241(13)	125(9)	-11(9)	76(8)	168(10)
C(5)	254(11)	217(13)	181(10)	-7(9)	82(8)	123(10)
C(6)	344(14)	184(14)	267(12)	81(10)	151(10)	124(11)
C(7)	288(12)	296(14)	203(10)	59(10)	98(9)	179(11)
C(8)	225(12)	243(14)	202(11)	-20(10)	50(9)	101(11)
C(9)	255(11)	219(13)	197(10)	1(9)	99(9)	130(10)
C(10)	292(13)	295(15)	219(12)	6(11)	70(10)	76(12)
C(11)	349(16)	401(19)	361(15)	175(14)	103(12)	181(15)
C(12)	317(14)	270(15)	248(13)	24(11)	80(10)	146(12)
C(13)	263(12)	343(15)	210(11)	40(10)	40(9)	193(11)
C(14)	277(13)	553(19)	330(13)	27(13)	20(10)	258(14)
C(15)	275(14)	580(20)	317(14)	1(13)	-74(11)	231(15)
C(16)	392(15)	371(16)	202(11)	49(11)	-32(10)	202(13)
C(17)	335(13)	351(15)	180(11)	78(10)	83(10)	189(12)
C(18)	251(12)	285(14)	192(10)	45(9)	19(8)	148(11)
C(19)	298(18)	1110(40)	550(20)	-30(20)	60(15)	360(20)
C(20)	500(20)	520(20)	220(13)	5(13)	-48(12)	249(18)
C(21)	224(12)	283(15)	204(11)	54(10)	61(9)	95(11)
C(22)	163(11)	340(15)	203(11)	-38(10)	8(8)	122(11)
C(23)	234(12)	359(16)	199(11)	-39(10)	-2(9)	202(12)

Table S.13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 21 (CCDC 612720).

	x	y	z	U_{iso}
H(2A)	5170(30)	10500(30)	8700(20)	35(8)
H(2B)	3880(40)	9200(40)	8820(30)	82(13)
H(3A)	2580(40)	9050(30)	7010(30)	54(9)
H(3B)	4200(30)	10280(30)	6830(20)	33(7)
H(6)	5630(30)	6470(30)	10640(20)	17(6)
H(8)	9170(30)	10250(30)	11210(20)	22(6)
H(10A)	3830(30)	5770(30)	7950(20)	31(7)
H(10B)	3130(30)	6560(30)	8560(20)	26(7)
H(10C)	3260(30)	5440(30)	9130(20)	28(7)
H(11A)	7610(30)	7450(30)	12520(20)	46(9)
H(11B)	8890(40)	9040(40)	12880(30)	64(10)
H(11C)	8980(40)	7800(30)	12040(30)	56(10)
H(12A)	8120(30)	11840(30)	9870(20)	41(8)
H(12B)	8180(30)	11090(30)	8730(20)	25(6)
H(12C)	9470(30)	11590(30)	9760(20)	39(8)
H(15)	310(30)	5890(30)	2910(20)	29(7)
H(17)	4570(30)	7010(30)	2890(20)	27(7)
H(19A)	620(30)	6450(30)	5820(30)	47(9)
H(19B)	-600(40)	6180(40)	4760(30)	67(10)
H(19C)	430(40)	7770(40)	5330(30)	82(13)
H(20A)	840(50)	5320(40)	1050(40)	98(15)
H(20B)	1850(40)	4730(40)	1210(30)	78(13)
H(20C)	2480(40)	6170(40)	840(30)	86(13)
H(21A)	6600(30)	9660(30)	5700(20)	32(7)
H(21B)	6730(30)	8670(30)	4650(30)	49(9)
H(22A)	8650(30)	8320(30)	6280(20)	31(7)
H(22B)	8200(30)	9140(30)	7370(20)	39(7)
H(23A)	7150(30)	6880(30)	7940(20)	41(8)
H(23B)	7580(20)	6170(20)	6823(18)	11(5)

Crystal Structure Analysis of 25

Contents



Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 177531.

Table S.15. Crystal data and structure refinement for 25 (CCDC 177531).

Empirical formula	$C_{36}H_{41}Cl_2N_5Ru$
Formula weight	715.71
Crystallization Solvent	Hexanes
Crystal Habit	Plate
Crystal size	0.33 x 0.28 x 0.08 mm^3
Crystal color	Orange

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000 CCD
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 15081 reflections used in lattice determination	2.35 to 28.09°
Unit cell dimensions	a = 11.3376(7) Å b = 13.3755(8) Å c = 21.4203(14) Å
Volume	3248.3(4) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	Pbcn
Density (calculated)	1.463 Mg/m^3
F(000)	1480
Data collection program	Bruker SMART v.5.054
θ range for data collection	1.90 to 28.26°
Completeness to θ = 28.26°	96.5 %
Index ranges	$-14 \le h \le 15$, $-17 \le k \le 17$, $-28 \le l \le 27$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	44246
Independent reflections	3886 [R_{int}= 0.0635]
Absorption coefficient	0.681 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9475 and 0.8064

Table S.15 (cont.)

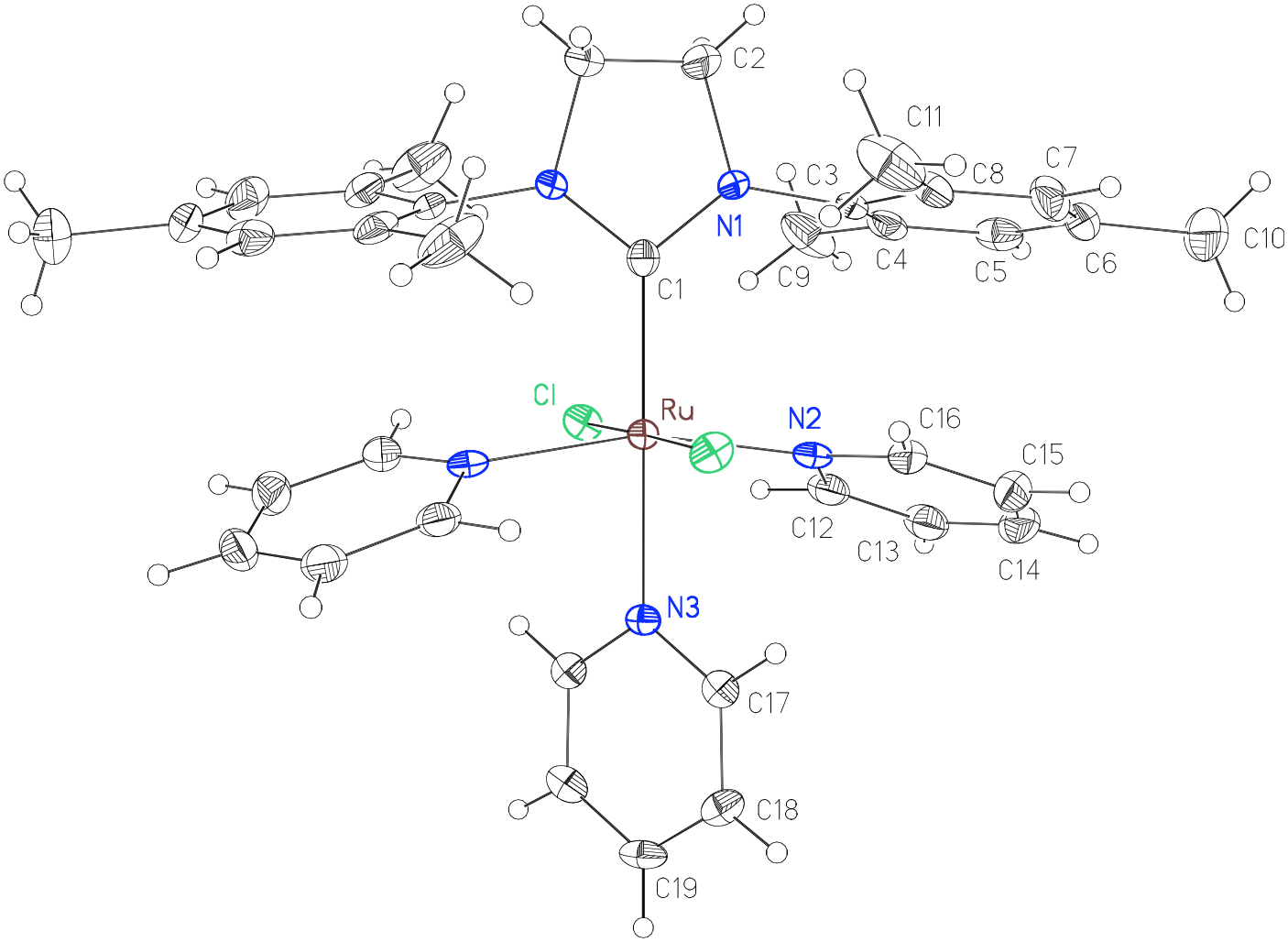
Structure solution and Refinement

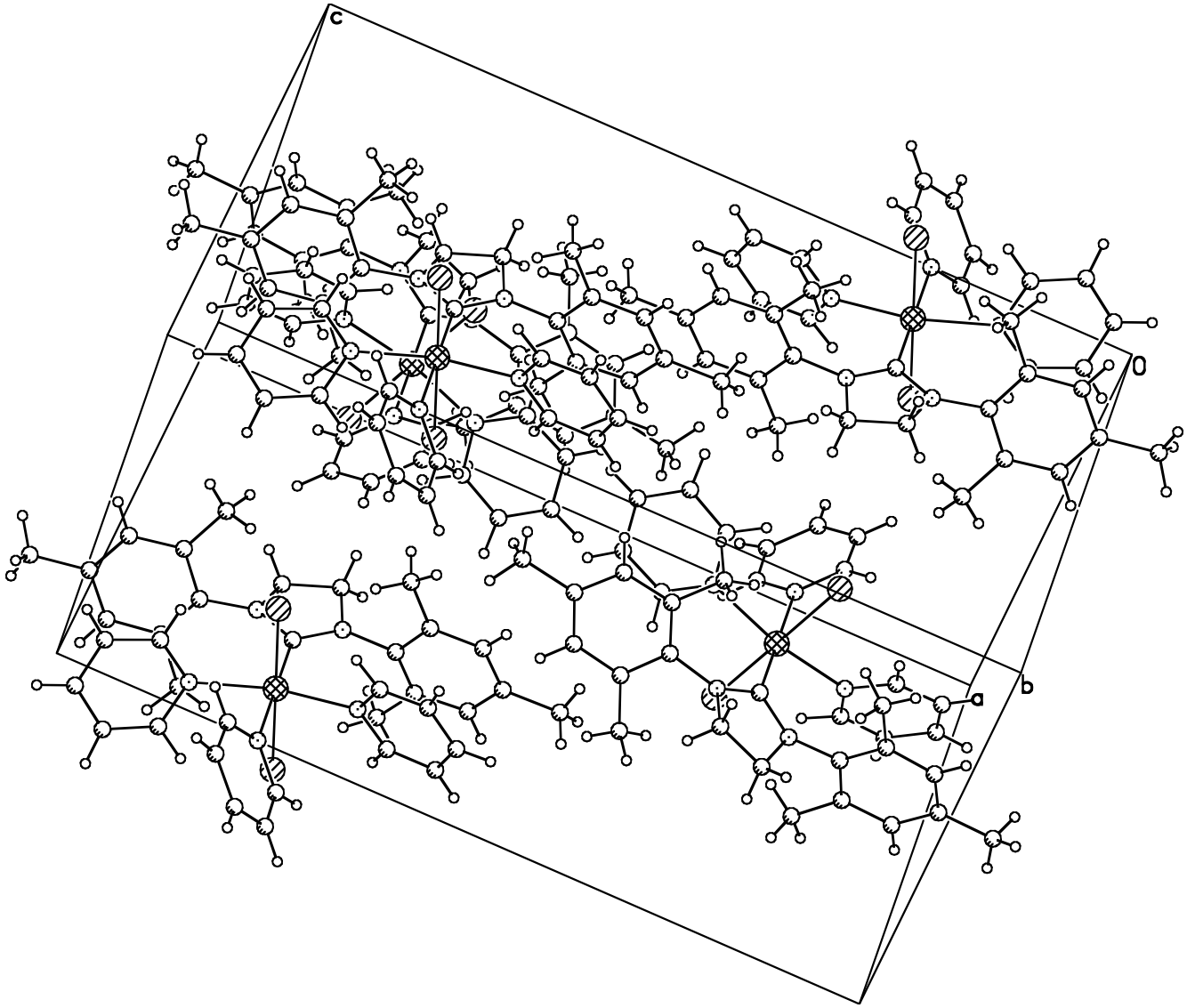
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3886 / 0 / 283
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.716
Final R indices [I>2σ(I), 2923 reflections]	R1 = 0.0320, *w*R2 = 0.0498
R indices (all data)	R1 = 0.0481, *w*R2 = 0.0509
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.006
Average shift/error	0.000
Largest diff. peak and hole	1.301 and -0.675 e.Å^{-3}

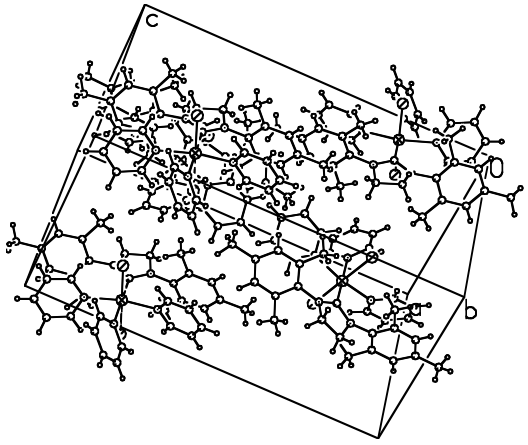
Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


C2
C11
C3
C8
C7
N1
C10
C9
C4
C5
C6
C1
Cl
Ru
N2
C16
C15
C12
C13
C14
N3
C17
C18
C19


c
0
a
b


c
0
b

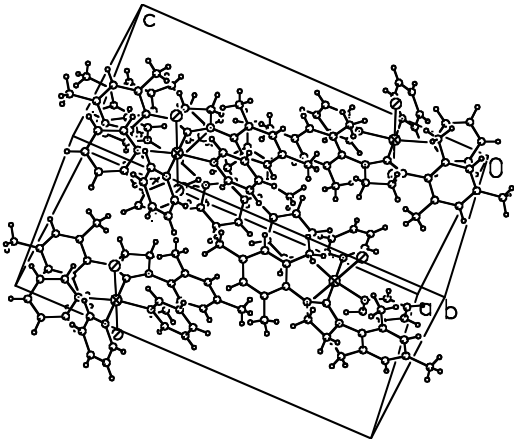

c
0
b

Table S.16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 25 (CCDC 177531). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru	10000	1639(1)	2500	12(1)
Cl	7966(1)	1621(1)	2874(1)	19(1)
N(1)	9783(2)	3805(1)	2009(1)	27(1)
N(2)	9421(2)	1420(1)	1566(1)	16(1)
N(3)	10000	13(2)	2500	13(1)
C(1)	10000	3174(2)	2500	16(1)
C(2)	9723(4)	4869(2)	2188(1)	58(1)
C(3)	9594(2)	3622(1)	1360(1)	19(1)
C(4)	8462(2)	3446(2)	1134(1)	21(1)
C(5)	8316(2)	3365(2)	494(1)	25(1)
C(6)	9242(2)	3482(2)	79(1)	27(1)
C(7)	10342(2)	3687(2)	322(1)	28(1)
C(8)	10546(2)	3762(2)	955(1)	22(1)
C(9)	7431(2)	3351(3)	1565(2)	39(1)
C(10)	9079(4)	3369(3)	-617(1)	53(1)
C(11)	11750(3)	3977(2)	1211(2)	43(1)
C(12)	8338(2)	1034(2)	1456(1)	24(1)
C(13)	7964(2)	701(2)	882(1)	29(1)
C(14)	8716(2)	743(2)	383(1)	32(1)
C(15)	9823(2)	1133(2)	477(1)	29(1)
C(16)	10130(2)	1456(2)	1064(1)	23(1)
C(17)	10613(2)	-515(2)	2076(1)	17(1)
C(18)	10634(2)	-1544(2)	2064(1)	20(1)
C(19)	10000	-2069(2)	2500	21(1)

Table S.17. Selected bond lengths [Å] and angles [°] for 25 (CCDC 177531).

Ru-C(1)	2.052(3)	C(1)-Ru-N(2)	97.92(4)
Ru-N(2)	2.1265(16)	C(1)-Ru-N(2)#1	97.92(4)
Ru-N(2)#1	2.1265(16)	N(2)-Ru-N(2)#1	164.16(8)
Ru-N(3)	2.176(2)	C(1)-Ru-N(3)	180.0
Ru-Cl	2.4415(5)	N(2)-Ru-N(3)	82.08(4)
Ru-Cl#1	2.4415(5)	N(2)#1-Ru-N(3)	82.08(4)
		C(1)-Ru-Cl	90.573(13)
		N(2)-Ru-Cl	90.88(5)
		N(2)#1-Ru-Cl	88.96(5)
		N(3)-Ru-Cl	89.427(13)
		C(1)-Ru-Cl#1	90.573(13)
		N(2)-Ru-Cl#1	88.96(5)
		N(2)#1-Ru-Cl#1	90.88(5)
		N(3)-Ru-Cl#1	89.427(13)
		Cl-Ru-Cl#1	178.85(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table S.18. Bond lengths [Å] and angles [°] for 25 (CCDC 177531).

Ru-C(1)	2.052(3)	C(1)-Ru-N(3)	180.0
Ru-N(2)	2.1265(16)	N(2)-Ru-N(3)	82.08(4)
Ru-N(2)#1	2.1265(16)	N(2)#1-Ru-N(3)	82.08(4)
Ru-N(3)	2.176(2)	C(1)-Ru-Cl	90.573(13)
Ru-Cl	2.4415(5)	N(2)-Ru-Cl	90.88(5)
Ru-Cl#1	2.4415(5)	N(2)#1-Ru-Cl	88.96(5)
N(1)-C(1)	1.371(2)	N(3)-Ru-Cl	89.427(13)
N(1)-C(3)	1.427(2)	C(1)-Ru-Cl#1	90.573(13)
N(1)-C(2)	1.475(3)	N(2)-Ru-Cl#1	88.96(5)
N(2)-C(12)	1.353(3)	N(2)#1-Ru-Cl#1	90.88(5)
N(2)-C(16)	1.343(3)	N(3)-Ru-Cl#1	89.427(13)
N(3)-C(17)#1	1.344(2)	Cl-Ru-Cl#1	178.85(3)
N(3)-C(17)	1.344(2)	C(1)-N(1)-C(3)	131.92(17)
C(1)-N(1)#1	1.371(2)	C(1)-N(1)-C(2)	113.84(18)
C(2)-C(2)#1	1.479(5)	C(3)-N(1)-C(2)	114.23(17)
C(2)-H(2A)	0.90(3)	C(12)-N(2)-C(16)	114.72(19)
C(2)-H(2B)	0.95(2)	C(12)-N(2)-Ru	119.76(14)
C(3)-C(4)	1.391(3)	C(16)-N(2)-Ru	124.28(15)
C(3)-C(8)	1.399(3)	C(17)#1-N(3)-C(17)	116.6(2)
C(4)-C(5)	1.386(3)	C(17)#1-N(3)-Ru	121.71(12)
C(4)-C(9)	1.496(3)	C(17)-N(3)-Ru	121.71(12)
C(5)-C(6)	1.384(3)	N(1)#1-C(1)-N(1)	103.9(2)
C(5)-H(5)	0.92(2)	N(1)#1-C(1)-Ru	128.03(11)
C(6)-C(7)	1.379(3)	N(1)-C(1)-Ru	128.03(11)
C(6)-C(10)	1.508(3)	N(1)-C(2)-C(2)#1	102.40(15)
C(7)-C(8)	1.380(3)	N(1)-C(2)-H(2A)	111.3(17)
C(7)-H(7)	0.94(2)	C(2)#1-C(2)-H(2A)	115.1(18)
C(8)-C(11)	1.499(3)	N(1)-C(2)-H(2B)	104.8(18)
C(9)-H(9A)	0.96(2)	C(2)#1-C(2)-H(2B)	114.8(17)
C(9)-H(9B)	0.86(3)	H(2A)-C(2)-H(2B)	108(2)
C(9)-H(9C)	0.97(3)	C(4)-C(3)-C(8)	121.16(19)
C(10)-H(10A)	0.89(3)	C(4)-C(3)-N(1)	120.50(19)
C(10)-H(10B)	0.89(3)	C(8)-C(3)-N(1)	117.76(19)
C(10)-H(10C)	0.98(4)	C(5)-C(4)-C(3)	117.99(19)
C(11)-H(11A)	0.99(3)	C(5)-C(4)-C(9)	120.7(2)
C(11)-H(11B)	0.88(2)	C(3)-C(4)-C(9)	121.3(2)
C(11)-H(11C)	0.93(2)	C(4)-C(5)-C(6)	122.3(2)
C(12)-C(13)	1.374(3)	C(4)-C(5)-H(5)	119.8(13)
C(12)-H(12)	1.02(2)	C(6)-C(5)-H(5)	117.8(13)
C(13)-C(14)	1.370(3)	C(7)-C(6)-C(5)	117.8(2)
C(13)-H(13)	0.97(2)	C(7)-C(6)-C(10)	120.2(3)
C(14)-C(15)	1.373(3)	C(5)-C(6)-C(10)	122.0(3)
C(14)-H(14)	0.94(2)	C(6)-C(7)-C(8)	122.5(2)
C(15)-C(16)	1.374(3)	C(6)-C(7)-H(7)	118.7(14)
C(15)-H(15)	0.929(19)	C(8)-C(7)-H(7)	118.8(14)
C(16)-H(16)	0.909(19)	C(7)-C(8)-C(3)	118.1(2)
C(17)-C(18)	1.377(3)	C(7)-C(8)-C(11)	121.8(2)
C(17)-H(17)	0.917(17)	C(3)-C(8)-C(11)	120.1(2)
C(18)-C(19)	1.372(3)	C(4)-C(9)-H(9A)	111.6(13)
C(18)-H(18)	0.911(18)	C(4)-C(9)-H(9B)	110.5(19)
C(19)-C(18)#1	1.372(3)	H(9A)-C(9)-H(9B)	110(2)
C(19)-H(19)	0.88(3)	C(4)-C(9)-H(9C)	111.5(17)
		H(9A)-C(9)-H(9C)	109(2)
C(1)-Ru-N(2)	97.92(4)	H(9B)-C(9)-H(9C)	104(2)
C(1)-Ru-N(2)#1	97.92(4)	C(6)-C(10)-H(10A)	108.7(18)
N(2)-Ru-N(2)#1	164.16(8)	C(6)-C(10)-H(10B)	113(2)

H(10A)-C(10)-H(10B)	106(3)	C(15)-C(14)-H(14)	119.5(13)
C(6)-C(10)-H(10C)	114(2)	C(13)-C(14)-H(14)	122.4(13)
H(10A)-C(10)-H(10C)	112(3)	C(16)-C(15)-C(14)	119.0(2)
H(10B)-C(10)-H(10C)	102(3)	C(16)-C(15)-H(15)	121.4(12)
C(8)-C(11)-H(11A)	112.1(19)	C(14)-C(15)-H(15)	119.6(12)
C(8)-C(11)-H(11B)	109.2(18)	N(2)-C(16)-C(15)	124.7(2)
H(11A)-C(11)-H(11B)	108(3)	N(2)-C(16)-H(16)	115.3(12)
C(8)-C(11)-H(11C)	113.4(15)	C(15)-C(16)-H(16)	120.1(12)
H(11A)-C(11)-H(11C)	105(2)	N(3)-C(17)-C(18)	123.2(2)
H(11B)-C(11)-H(11C)	110(2)	N(3)-C(17)-H(17)	116.6(11)
N(2)-C(12)-C(13)	124.0(2)	C(18)-C(17)-H(17)	120.2(11)
N(2)-C(12)-H(12)	113.9(13)	C(19)-C(18)-C(17)	119.3(2)
C(13)-C(12)-H(12)	122.1(13)	C(19)-C(18)-H(18)	122.2(12)
C(12)-C(13)-C(14)	119.5(2)	C(17)-C(18)-H(18)	118.4(12)
C(12)-C(13)-H(13)	116.3(13)	C(18)#1-C(19)-C(18)	118.5(3)
C(14)-C(13)-H(13)	124.2(13)	C(18)#1-C(19)-H(19)	120.77(14)
C(15)-C(14)-C(13)	118.0(2)	C(18)-C(19)-H(19)	120.77(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table S.19. Anisotropic displacement parameters ($Å^2 x 10^4$) for 25 (CCDC 177531). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru	106(1)	119(1)	131(1)	0	4(1)	0
Cl	129(2)	200(3)	233(3)	30(2)	28(2)	14(2)
N(1)	550(14)	111(8)	136(9)	-13(7)	-42(9)	35(9)
N(2)	173(9)	92(9)	226(10)	18(7)	7(8)	5(7)
N(3)	105(10)	126(11)	171(11)	0	-42(12)	0
C(1)	149(13)	191(15)	150(13)	0	13(15)	0
C(2)	1350(40)	160(13)	228(14)	-24(11)	-170(20)	88(19)
C(3)	302(13)	101(11)	152(11)	25(8)	-23(9)	24(8)
C(4)	235(12)	138(11)	257(12)	57(10)	34(9)	71(10)
C(5)	237(13)	169(11)	341(14)	22(11)	-134(10)	17(11)
C(6)	434(16)	206(13)	169(12)	29(10)	-45(10)	38(11)
C(7)	308(15)	282(14)	243(13)	69(10)	116(10)	16(10)
C(8)	231(12)	181(12)	239(13)	69(10)	-26(10)	-20(9)
C(9)	321(16)	351(16)	493(18)	204(16)	183(13)	163(15)
C(10)	920(30)	430(20)	229(15)	-24(16)	-156(17)	40(20)
C(11)	299(17)	406(19)	580(20)	197(17)	-112(16)	-88(14)
C(12)	296(14)	154(12)	277(14)	34(10)	-71(11)	-19(10)
C(13)	373(15)	192(12)	309(15)	36(10)	-125(12)	-42(11)
C(14)	507(18)	222(13)	239(15)	-46(11)	-143(13)	71(12)
C(15)	399(17)	261(13)	212(13)	-10(10)	12(12)	88(12)
C(16)	304(14)	171(12)	218(11)	-2(8)	-12(11)	42(12)
C(17)	117(11)	197(12)	192(12)	7(10)	-22(9)	0(9)
C(18)	146(11)	202(12)	263(12)	-62(11)	-35(10)	28(10)
C(19)	181(15)	116(14)	346(17)	0	-98(17)	0

Table S.20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 25 (CCDC 177531).

	x	y	z	U_{iso}
H(2A)	10080(20)	5260(20)	1902(12)	54(8)
H(2B)	8900(20)	5030(20)	2185(12)	63(11)
H(5)	7582(18)	3213(15)	332(9)	27(6)
H(7)	10978(19)	3783(15)	44(10)	33(7)
H(9A)	7607(18)	2928(16)	1914(10)	29(6)
H(9B)	7210(20)	3930(20)	1693(13)	68(10)
H(9C)	6740(30)	3090(20)	1352(13)	67(10)
H(10A)	8320(20)	3410(20)	-703(12)	57(10)
H(10B)	9320(30)	2780(30)	-759(14)	81(12)
H(10C)	9550(30)	3840(30)	-866(17)	115(15)
H(11A)	11800(30)	4650(20)	1402(14)	88(12)
H(11B)	12270(20)	3950(20)	908(12)	50(9)
H(11C)	11970(20)	3544(18)	1527(11)	44(8)
H(12)	7820(20)	992(16)	1843(11)	43(7)
H(13)	7176(19)	426(16)	865(10)	36(7)
H(14)	8486(18)	552(15)	-22(10)	27(6)
H(15)	10349(17)	1169(15)	145(9)	20(6)
H(16)	10857(17)	1721(14)	1133(8)	14(5)
H(17)	11027(15)	-156(13)	1786(8)	9(5)
H(18)	11099(16)	-1853(13)	1775(9)	12(5)
H(19)	10000	-2720(20)	2500	19(7)